Study of APS and conventional sintering parameters for the manufacture of TiO$_2$ targets for PAPVD

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Abstract. In surface science of functional oxides, titanium dioxide (TiO$_2$) is one of the most investigated crystalline systems either in rutile or anatase phases. In this work commercial TiO$_2$ powders are used to study the required process conditions to obtain TiO$_2$ targets by Atmospheric Plasma Spray (APS) and conventional sintering, with suitable physical and chemical properties to be source material for Plasma Assisted Physical Vapor Deposition (PAPVD) for technological and medical applications. Two three factor Box Behnken experimental designs combined with surface modeling were employed to estimate the influence of spraying parameters (gun current, Ar/H$_2$ ratio and standoff distance) and sintering parameters (heating rate, sintering temperature and holding time) within the target microstructure (cracks and pores in cross section) and phases composition. The microstructure and composition of APS-deposited targets and sintered ones were characterized by Scanning Electron Microscopy (SEM) and X-Ray Diffraction (XRD). The lowest defects percentages of the targets manufactured in this work were 0.41 ± 0.30% for APS-deposited targets and 0.05 ± 0.04% for the sintered ones using the optimal parameters suggested by the statistical model, which allowed confirming the advantages of sintering process and limitations of APS in terms of microstructural homogeneity, but also of the use of design of experiments in the modeling of systems of many variables when there is not diagnostic equipment of the processes available.

1. Introduction

The manufacture of thin films for technological and high performance applications are issues that on a global scale have marked the greatest scientific and technological advances in microelectronics, telecommunications, biomedical, optical, among other applications [1]. The production of thin films by plasma-based techniques includes PAPVD processes in which, the coating is formed by the transport of species detached from a piece called “target” towards a substrate inside a reactor under high vacuum atmosphere that promotes the formation of the plasma (reactive or non-reactive) [2].

In addition to the logistical advantages that offers the self-supply of components such as targets inside the laboratory for PAPVD processes, it is important to have a rigorous control over its quality because, for example: i) the targets superficial microstructure is related to the structure, uniformity and quality of the thin films [3], ii) dense targets contribute to increase the deposition rate and exhibit a more stable resistivity [4] and iii) large average grain sizes of the targets (greater than 50 µm) combined with small target-substrate distances (around 5 cm) affect the homogeneity of the thin film and can cause target detachments [5], among others.
According to the above, to advance in the production of higher quality coatings, researchers have had to ensure the high performance and efficiency of the targets, specifically, meet requirements such as: purities between 99 and 99.99 %, grain sizes not greater than 50 μm and densities of 99.9 % or greater [6]. For all these reasons, the importance of studying the types of targets processing and its parameters influence on their quality is currently identified, since their characteristics depend on it [7].

This research was focused on manufacturing targets of one of the most investigated crystalline systems, the TiO$_2$ [8], first by conventional sintering, and then by APS in order to compare and analyze the results to select the technique and manufacturing conditions that allow to obtain targets with suitable physical and chemical properties to be source material for PAPVD coatings in technological and medical applications.

2. Materials and methods

One of the main factors in the manufacture of the targets is the raw material. Table 1 presents the feedstock powders used in the experimental tests and its different characteristics. The previous powders were processed by conventional sintering and APS to obtain targets.

Conventional sintering is used to form solid parts from powders and involves compacting powders in a specific form, green compact, and then increasing the temperature of the green compact. The manufacture of targets by conventional sintering required the use of an automated Accu-tek Touch 500 press of the ELE International brand to compress the raw powders, a furnace of maximum temperature 1700 °C of the Nabertherm brand and a controlled atmosphere tubular furnace of maximum temperature 1700° C of the Carbolite brand. The Fixed Parameters for sintering (FP$_{sint}$) were: desionised water as compression binder for the Oerlikon Metco powders, no raw materials doping with Nb$_2$O$_5$, pressing rate 0.48 MPa/s, compression force 500 kN (250 MPa), an isotherm at 130 °C for 2 hours was used, heating rate 5 °C/min from 130 °C, sintering temperature 1500 °C, holding time 4 hours, sintering atmosphere air and cooling rate of 1.6 °C/min; the sintering parameters that were varied in each test are indicated in each section of the results.

On the other hand, APS is one of the thermal spray techniques within which the raw material is deposited in a molten or semi-molten condition to form the thick layer, to manufacture the targets by APS, a Sulzer Metco MultiCoat system equipped with a F4MB torch was used. The fixed parameters for APS (FP$_{APS}$) were: feedstock Metco 102, powder mass flow rate 30 g/min, carrier gas Ar 5 L/min at 4 bar, anode nozzle i.d. 6 mm, substrate material XC-38 Carbon Steel, temperature of preheated substrates 300 °C, substrate roughness 7.76 ± 0.81 μm, robot movement at 24 mm/s in translation and 1 m/s in rotation, projection time 5 minutes. The parameters variation in both processes sintering and APS are presented in the results section.

The evaluated targets properties were microstructural homogeneity (percentage of pores and cracks in cross section) and phases composition. The targets samples were cut, mounted on resin, polished to a mirror finish and prepared metalographically to evaluate, in their cross section, the microstructure. The defects percentage was the average of the values processed with the ImageJ software of 20 micrographs taken at each target in cross-section using Scanning Electron Microscopy (SEM) with a JEOL JSM-7400F microscope. The identification of the present phases in both raw powder and manufactured targets was carried out using X-Ray Diffraction (XRD) with a XPert PANalytical Empyrean Series II Alpha1 diffractometer and a Bruker D8 Advance diffractometer and with the software X'Pert HighScore Plus and the ICSD database. A power source and nanovoltmeter were used to measure the electrical resistivity of the sintered targets by four point probe technique at room temperature and a Buehler Micromet 6040 durometer was used to determine the Vickers microhardness (using 0.2 kg) of the APS-deposited targets. The statistical analyses were carried out with Statgraphics software.
Table 1. Feedstock particles characteristics, DuPont R-902 from DuPont, United States and Metco 6231A, Metco 102 and Amdry 6510 from Oerlikon Metco, Switzerland.

| Reference     | Particle Size Distribution, PSD -d10 +d90 [µm] (PSD type) | Synthesis (morphology) | Composition          |
|---------------|------------------------------------------------------------|-------------------------|----------------------|
| DuPont R-902  | -103 +0.76 (bimodal, nano and micrometric)                 | Crushed (angular)       | TiO$_2$ (93 % p/p)   |
| Metco 6231A   | -105 +32 (monomodal, micrometric)                          | Sintered (spherical)    | TiO$_2$ (99 % p/p)   |
| Metco 102     | -45 +11 (monomodal, micrometric)                           | Crushed (angular)       | TiO$_{1.9}$ (99 % p/p) |
| Amdry 6510    | -106 +38 (monomodal, micrometric)                          | Crushed (angular)       | TiO$_{1.9}$ (99 % p/p) |

3. Results and discussion

3.1. Parameters identification

The results of the identification of the parameters that affect to a greater extent the microstructure of the targets manufactured by conventional sintering are summarized in Table 2 in a descending way, the most significant effect was produced by changing the PSD of the raw material, using a narrow PSD (-45 +11 µm) and then a wide one (-103 +0.76 µm) leaving the other parameters fixed (described in the methodology as FP$_{set}$) managed to vary the percentage of defects measured in 15.63%; while varying from 3 to 12 hours the time in which the green piece was held at the sintering temperature only reached to produce a change of 0.68% in the percentage of defects. In Table 2 each row contains the information of two experiments, in the first column the parameter that was being evaluated with the realization of the two experiments, in the second column the two values that the parameter in evaluation took, in the third column the result of subtracting the percentage of defects of the two obtained samples and the percentage of defects of one of the two samples (the smaller of the two percentages) with their standard deviation, and in the last column the information about the other manufacturing parameters, which were the same for both experiments. The last row shows the result of the percentage of defects of two targets manufactured on different days with the same conditions and parameters, the difference in the percentage of both samples was 0.025%.

The composition in phases of the raw materials are presented in Figure 1 and evidences that Metco 102, Metco 6231A and Amdry 6510 powders contain several phases, in addition to those reported by the manufacturer; while the DuPont R-902 powder contains only rutile. On the other hand, the targets manufactured by sintering contain only rutile regardless of the raw powder and used process parameters, Figure 2 presents the diffractograms of some different samples manufactured for the identification of the effects of the parameters, of a green compact and in vertical lines it is indicated the Bragg reflections of a reference pattern of rutile.

The identification of the effects of the APS parameters on the microstructure of the targets was also carried out varying a single factor while keeping all the other factors fixed. Table 3 summarizes the results in the same format as Table 2. The proportion of plasmogenic gases produced the most significant effect because, even with 5 minutes projection times, no coatings greater than 10 microns were obtained when 0% H$_2$ was used as secondary gas, regardless of the current used (400 or 650 A) or the standoff distance (SOD) (130 or 70 mm), the values that could not be calculated due to the low thickness of the coatings are indicated by a dash.

The targets manufactured by APS contain mainly rutile, the remaining content corresponds to anatase and other Magneli phases (Ti$_x$O$_{2n-1}$), Figure 3 and Figure 4. Anatase is a metastable phase and its transformation into rutile occurs at temperatures between 400 ºC and 1200 ºC depending on its physicochemical characteristics and exposure conditions [9]. Rutile, on the other hand, has a Gibbs free energy (ΔG) more negative than anatase, so the transformation of anatase into rutile under projection conditions becomes irreversible [10], [11]. During the thermal plasma projection process at atmospheric pressure, the temperatures involved are those at which the conversion of anatase to rutile occurs [12].
Table 2. Analysis in porosity of some parameters involved in the manufacture of targets by conventional sintering.

| Parameters evaluated          | Parameter variation | Defects [%] | Fixed conditions                                      |
|------------------------------|---------------------|-------------|-------------------------------------------------------|
| Sintering temperature        |                     |             |                                                       |
| Fixed conditions             |                     |             |                                                       |
| Sintering temperature        | 850 → 1450          | -           | 0.27 ± 0.13                                           |
| 1500 °C → 1200 °C           |                     | 7.19        | 14.14 ± 0.30                                          |
| 1500 °C → 1200 °C           |                     | 4.75        | 0.70 ± 0.16                                           |
| 1200 °C → 1500 °C           |                     | 3.79        | 20.22 ± 1.47                                          |
| PSD                         | -45 +11 → -103 +0.76| 15.63       | 5.45 ± 0.36                                           |
| -45 +11 → -106 +38          |                     | 12.93       | 8.15 ± 1.39                                           |
| Sintering atmosphere         | argon and air → air | 15.05       | 5.45 ± 0.36                                           |
| air → argon and air          |                     | 4.03        | 6.47 ± 0.55                                           |
| Doping with Nb2O5            | without → 2 % wt.   | 14.03       | 6.47 ± 0.55                                           |
| 2 % wt. → without           |                     | 5.05        | 5.45 ± 0.36                                           |
| Particles morphologies       | spheroidal → angular| 13.18       | 8.15 ± 1.39                                           |
| Compression binder           | H2O → without PVA   | 4.77        | 16.56 ± 0.54                                           |
| Compression force            | 750 MPa → 125 MPa   | 1.18        | 19.04 ± 1.16                                           |
| Heating rate                 | 1 °C/min → 10 °C/min| 1.21        | 0.60 ± 0.13                                           |
| Holding time                 | 3 hours → 1 hour    | 3.85        | 0.56 ± 0.13                                           |
| 3 hours → 12 hours           |                     | 0.68        | 13.46 ± 1.12                                          |
| 4 hours → 12 hours           |                     | 0.21        | 0.49 ± 0.27                                           |
| 2 hours → 1 hour             |                     | 0.41        | 0.18 ± 0.07                                           |
| 1 hour → 3 hours             |                     | 0.04        | 0.06 ± 0.04                                           |
| Heating rate                 | 1 °C/min → 10 °C/min| 0.58        | 0.19 ± 0.08                                           |
| 10 °C/min → 1 °C/min         |                     | 0.05        | 0.06 ± 0.04                                           |
| Compression force            | 750 MPa → 125 MPa   | 1.18        | 19.04 ± 1.16                                           |
| Short-term repeatability     | day 1 → day 2       | 0.02        | 0.05 ± 0.04                                           |
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**Figure 1.** Feedstock XRD spectra.

**Figure 2.** XRD spectra of some sintered targets.
Table 3. Analysis in porosity of some parameters involved in the manufacture of targets by APS.

| Parameters evaluated | Parameter variation | Defects [%] | Fixed conditions |
|----------------------|---------------------|-------------|-----------------|
|                      | Decrease | Final amount |                 |
| **Ar/H₂ rate**       | 60/00 → 40/20 | - | 0.87 ± 0.18 | 400 A (650 A), 100 mm, FPₐₚₛ |
|                      | 81       | 0.94 ± 0.41  | 525 A, 130 mm (70 mm), FPₐₚₛ |
| **Standoff distance**| 40 mm → 70 mm | - | 0.89 ± 0.22 | 600 A, 46/14, FPₐₚₛ |
|                      | 70 mm → 130 mm | 1.01 | 0.94 ± 0.41 | 525 A, 40/20, FPₐₚₛ |
|                      | 130 mm → 70 mm | 0.60 | 0.90 ± 0.12 | 400 A, 50/10, FPₐₚₛ |
|                      | 130 mm → 130 mm | 0.52 | 0.41 ± 0.30 | 650 A, 50/10, FPₐₚₛ |
| **Carrier gas flow rate** | 3 L/min → 5 L/min | 2.00 | 0.55 ± 0.19 | 525 A, 50/10, 100 mm, FPₐₚₛ |
| **Current**           | 400 A → 650 A | 1.09 | 0.41 ± 0.30 | 50/10, 70 mm, FPₐₚₛ |
|                      | 650 A → 400 A | 0.03 | 0.90 ± 0.12 | 50/10, 130 mm, FPₐₚₛ |
|                      | 650 A → 400 A | 0.94 | 0.87 ± 0.18 | 40/20, 100 mm, FPₐₚₛ |
| **PSD**               | -45 +11 → 106 +38 | 0.96 | 0.89 ± 0.22 | 600 A, 46/14, 70 mm, FPₐₚₛ |
| **Short-term repeatability** | day 1 → day 2 | 0.06 | 0.49 ± 0.16 | 525 A, 50/10, 100 mm, FPₐₚₛ |

**Figure 3.** XRD spectra of the targets manufactured by APS at low torch powers.
Figure 4. XRD spectra of the targets manufactured by APS at high torch powers.

3.2. Parameters optimization

Identified the most significant manufacturing parameters of both techniques in relation to the percentage of defects of the targets, new experiments were carried out to complete for each technique a matrix of 15 experiments proposed by the statistical design of experiments called Box-Behnken. Table 4 presents the parameters (factors) and values (levels) used in the designs, which allow not only to graph the effects of the parameters evaluated and their interactions from contour or surface graphs such as those presented in Figure 5, but to create a quadratic model of each system (sintering and APS) and optimize the studied property, percentage of defects (response).

The relationships between dependent and independent variables are displayed from contour or surface graphs. Since the design has three factors, one of the three factors remains constant at the central level for each graph and one response is plotted three dimensionally versus the other design factors. Figure 5 shows two three dimensional response surfaces and the corresponding contour graphs for defects percentage. For example, Figure 5.a shows that the sintering time has a light effect on the defects percentage compared to the sintering temperature and Figure 5.b shows how the defects percentage decreases as consequence of increasing the standoff distance and decreasing the current.

Table 4. Parameters and values selected for the Box-Behnken designs.

| Manufacturing process | Factor                        | Lower level | Central level | Upper level |
|-----------------------|-------------------------------|-------------|---------------|-------------|
| Sintering             | Heating rate [°C/min]         | 1           | 5             | 10          |
|                       | Holding time [horas]          | 1           | 2             | 3           |
|                       | Sintering temperature [°C]    | 800         | 1150          | 1500        |
| APS                   | Standoff distance (SOD) [mm]  | 70          | 100           | 130         |
|                       | Current [A]                   | 400         | 525           | 650         |
|                       | Ar ratio [%]                  | 66.7 (40/20)| 83.3 (50/10)  | 100.0 (60/00)|
Figure 5. Estimated response surfaces showing the combined effect on the defect percentage of: a. holding time and sintering temperature when the heating rate is 5 °C/min and b. standoff distance and current when the Ar ratio is 83.35 % (Ar/H₂ = 50/10).

By generating surface graphics with a statistical software, the optimal factors or parameters are located with reasonable precision by characterizing the shape of the surfaces. Table 5 presents the optimal responses or properties of the targets estimated by the statistical designs (minimum percentage of defects and in addition maximum thickness and micro hardness for the projected targets) and the parameters proposed by the models to achieve the desired responses. Table 6 summarizes the parameters experimentally used and the obtained properties.

Although these response values are not those predicted by the statistical designs, or the best obtained in the work, in the case of sprayed targets, the statistical designs proved to be an approach to modeling this type of complex systems.

Table 5. Optimum factors and response estimated by the Box-Behnken designs.

| Manufacturing process | Estimated optimum responses | Estimated optimum factors |
|-----------------------|-----------------------------|---------------------------|
|                       | Rate [°C/min] = 5.0          |                           |
|                       | Ar ratio [%] = 83.35         |                           |
|                       | Time [horas] = 1.99          |                           |
|                       | Rate Temperature [°C/min] = 1152.12 |                |
|                       | Defects Thickness Micro Hardness [µm] [GPa] | |
| Sintering             | 0.001 902.5 11.64           | 5.04 1.99 1152.12         |
| APS                   | 0.62 902.5 11.64            | 70.19 603.16 76.37        |

Table 6. Used optimum factors and obtained responses.

| Manufacturing process | Used optimum factors | Obtained optimum responses |
|-----------------------|----------------------|-----------------------------|
|                       | Rate Time Temperature | Defects Thickness [°C/min] [horas] [°C] [%] [µm] |
| Sintering             | 5 2 1150             | 0.049 767.34                |
|                       | SOD Current Ar Ratio |                           |
|                       | 70 600 76.3          | 1.85 767.34                |

(a) (b)
Figure 6. Defects percentage of targets manufactured by: a. and c. conventional sintering from DuPont R-902 powder and the conditions indicated on the image, b. and d. APS from Metco 102 powder and the conditions indicated on the image.

4. Conclusions
The effects in the targets properties can be as varied as the combinations of manufacturing parameters therefore it is evident the need to apply experimental designs, which exist to visualize this type of effects and interactions and allow to have models of the systems for the control of the properties to obtain, especially when there are no diagnostic devices for the processes and these consist of black boxes.

The raw materials from which the targets with lower percentage of defects could be obtained were determined as well as the manufacturing parameters to be optimized based on the identification of the parameters that have a more significant effect in the defects percentage of the targets, the sintering temperature, holding time and heating rate for conventional sintering and the ratio of plasmogenic gases, standoff distance and current for APS.

The targets manufactured by sintering with the lower defects percentage (0.05 ± 0.04 %) were obtained using the bimodal feedstock powder (DuPont -103.32 µm +0.76 µm) at 5 °C/min to 1150 °C for 2 hours in air atmosphere. The APS thermally sprayed targets with the lower defects percentage (0.41 ± 0.30 %) and higher hardness values (10.8 ± 0.6 GPa) were obtained by using the monomodal feedstock powder (Metco 102 -53.17 µm +16.13 µm) at 70 mm using a plasma generated by a Ar/H₂ of 50/10 NL/min and 650 A. The above allowed confirming the advantages of sintering and limitations of APS in terms microstructural homogeneity in order to choose the best option to manufacture targets for PAPVD coatings for technological and medical applications.

The manufactured targets are composed mostly of rutile, phase of which tribological applications and transparent conductors when it is doped are reported, however, it is also reported that from targets composed of rutile it is possible to develop applications of the anatase phase, based on its biocompatibility and photocatalysis, if the thin films are heat treated after being sputtered.

Some specific advantages identified during the project execution about the manufacture of targets in the laboratory are suitable cost/ benefit relationship and be able to have useful information about the characteristics of the target, such as microstructure (defects) and phases composition.
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