https://doi.org/10.2352/ISSN.2470-1173.2017.8.MAAP-278

Study of the influence of roughness on the gonioapparency of anodized titanium

CRIDLING Quentin[1,2], CHARRIERE Renee[1,3], JAMON Damien[4], DIAMANTI Maria Vittoria[2], PEDEFERRI Maria Pia[2], DELAFOSSE David[1,2] ; [1]Ecole Nationale Superieure des Mines de Saint-Etienne, SMS EMSE, CNRS UMR5307, Laboratoire Georges Friedel; Saint-Etienne, France; [2]Politecnico di Milano, Department of Chemistry, Materials and Chemical Engineering "Giulio Natta" ; Milan, Italy; [3]National Institute of StandardStudy of the s and Technology; Gaithersburg, MD,United States; [4]Laboratoire Hubert Curien CNRS, UMR5516, Université de Lyon, Université de Saint-Etienne, Jean Monnet, F-42000, Saint-Etienne, France.

Abstract

The visual impact of a product plays a key role in the consumer-perceived quality of the product. Coatings are a good solution to improve the quality of a product by either changing its appearance or add a new property, such as corrosion protection.

Anodized titanium exhibits a wide range of colors, and in some cases gonioapparency, that is color changes depending on the observation and/or the illumination directions. It also offers other properties such as corrosion protection or photocatalysis.

With the development of goniospectrophotometers, the colors of gonioapparent anodized titanium can be characterized but the parameters influencing the color or its gonioapparency remain unclear. The present study focuses on the influence of the roughness on the color of anodized titanium samples through measurements and optical modeling. Colors have been characterized through BRDF measurements but future comparisons between measured and perceived colors are planned. A specific device dedicated to these perception tests has been designed and is presented in the present paper.

I - Introduction

Oxidized titanium is well known in the literature for its numerous interesting properties such as photocatalytic properties [1] that can be used in self-cleaning applications [2], for its resistance to corrosion and also for its interferential coloration [3].

Titanium oxidation can be obtained through various techniques such as heating [3], laser irradiation [4], anodizing [5] or even mixed methods [6]. Only anodizing will be explored in the present document.

Anodizing, or anodic oxidation, allows the growth of a controlled oxide layer in thickness, structure, color, crystallinity and electrical properties. These properties are driven by the experimental parameters such as the current density, the cell potential, the electrolyte composition and temperature [5][7]. The resulting color of the sample can vary on a wide gamut and this property leads to applications in the field of design, architecture [8] and jewelry [3]. These colors rely on the production of a thin oxide film with a thickness ranging from a few tens of nanometers to about two hundred nanometers. It corresponds to the same order of magnitude of the visible wavelengths, which is essential to the occurrence of the interferential phenomenon in the visible spectrum. In some cases, the colors of anodized titanium samples have the particularity to vary according to the illumination and observation directions. Such samples are said to be gonioapparent.

Gonioapparent materials show a significant growth in their usage in many industrial sectors, such as automotive painting, architecture or the luxury industry. Those materials are difficult to characterize and their color quality control remains challenging because their color is characterized by an optical path in the CIE xy chromaticity diagram (not a unique point) and because of the lack of gonioapparent reference color charts. Anodized titanium is a promising material for building a gonioapparent reference color chart. A preliminary study [9] shows that its color chromatic paths can be modified through the anodizing conditions and/or the roughness of the surface.

In the present study, samples with an initial roughness ranging from about 10 nm to about 200 nm were prepared to investigate the influence of the roughness on the color of anodized titanium and on the gonioapparence of the material. An experimental setup to perform perception tests of the gonioapparence of the anodized titanium samples has also been designed. This experimental setup can be used to observe samples with the same geometries as commercial multi-angle spectrophotometers but isn't limited to those angles and can be used to explore a wide range of different geometries.

II – Samples preparation and selection

II – A] Sample polishing

Experiments were carried out on commercially pure ASTM grade 2 titanium samples. This classification means that the maximum impurities percentage are O< 0.25% – N < 0.03% – H < 0.015% – Fe< 0.3%. Samples were cut out of a 1 mm thick titanium sheet.

To explore the influence of the roughness of the raw material on the color of anodized samples, three different series of samples were prepared. A rotating sample holder (with a rotation axis different from the rotation axis of the grinding machine) was used to avoid a periodicity in the scratches formed during the grinding process and also to randomize the directions of those residual scratches. A simple polishing with a P300 grinding paper was used for the first batch; these samples will be called "P300". This step is also crucial to obtain plane surfaces and remove initial defects. The mirror finishing of the second batch has been obtained by a complete mechanical polishing (with successively P300, P1200, P2400 and P4800 grinding papers) and a final step using a grinding cloth and an alumina solution with particle size of 0.6 µm; those samples will be referred as "Alumina". Instead of using the alumina solution, the samples of the last series were polished with 6µm, 3µm and 1µm diamond paste solution. To further decrease the surface roughness a vibratory polisher Buehler Vibromet2 and a 60 nm colloidal solution were used to obtain the last series designed further as "Vibrometer".

II – B] Anodizing method

In the literature, a preliminary etching in an HF/HNO_3 solution has been shown to slightly promote titanium oxidation, i.e. the thickness of the oxide layer is higher on an etched sample than

on a non-treated sample when the same potential is applied. It also improves visually the homogeneity of the color [10]. In reference [11], Lamolle and al showed the presence of fluorine on the surface of a titanium sample that has been exposed to a hydrofluoric acid solution. The effect on the anodized sample color of the presence of fluorine on the surface of the titanium substrate remains unknown. To observe the sole influence of the roughness on the color of anodized samples, anodizing was performed without a preliminary HF etching.

Anodizing was carried out in galvanostatic regime by imposing a current density equal to 20mA/cm² and at maximum potential values ranging from 10V to 130V. All experiments were performed in a 0.5 mol sulfuric acid electrolytic solution (H_2SO_4) and at room temperature. The experiment is immediately stopped when the expected potential is reached.

II – C] Samples selection

P300 samples were observed with the naked eye and rotated slowly from 0° (horizontal position) to 90° (vertical position) to roughly detect the gonioapparent nature of each sample. The samples were sorted out in three categories and one sample of each category has been selected:

- non gonioapparent, the color remains visually the same during all the rotation. The sample anodized at 10V has been selected.
- gonioapparent at small angle, the color changes with a small variation of the angle, smaller than 45°. The sample anodized at 20V has been selected.
- gonioapparent at high angle, the color changes with a big variation of the angle, bigger than 45°. The sample anodized at 90V has been selected.

III – Samples characterizations

III – A] Roughness measurements

Roughness measurements have been carried out by a non-contact white light interferometric optical profilometer, Bruker Nanoscope Wyko ® NT9100. The roughness has been measured before anodizing to obtain the roughness of the titanium substrate and after anodizing to characterize the roughness of the oxide layer. The size of the measured area is 0.86mm x 1.15mm (representing 480x640 points) with a resolution of 1.8 µm in both in-plane directions and a vertical resolution of 3nm.

For each sample, five measurements have been made around the center of the sample on an area of about 0.5x0.5 cm to obtain a resilient assessment of the roughness on this area. The center of the sample is indeed the area characterized by the goniospectrometric measurements. To monitor the homogeneity of the surface sample, at least four additional measurements were performed on each sample, at each corner and at some randomly chosen areas. It is important to notice that the roughness results were the same (in the error bars) with and without any numerical correction as for example tilt removal or higher order polynomial corrections.

In the table 1, the average roughness parameters R_a have been represented. The R_a parameter is the arithmetic average on the observed area of the absolute values of the difference between the height of a point and the average height of the surface. The material is considered isotropic so the R_a (1 dimension parameter averaged on the observed area) and the S_a (2 dimension parameter) can be considered equal in this case. Other roughness parameters were also collected but not discussed in the present document. The indicated uncertainty is a repeatability uncertainty corresponding to the maximal deviation from the average value. "Substrate" corresponds to a measurement made before anodizing, "Anodized" to a measurement made after anodizing, "C" to measurements made in the center of the sample and "S" to the additional measurements made all over the surface (center measurements excluded). Roughness measurements of the titanium substrate revealed that the preparation of the samples was homogeneous for the all three series and three ranges of substrate roughnesses. We obtain average R_a parameters of 15 nm, 60 nm and 230 nm respectively for Vibrometer, Alumina and P300 series.

Table1: Roughness parameters R_a before and after anodizing.

	R_a P300	R_a Alumina	R_a Vibrometer
10V Substrate	C: 215 ± 5 nm S: 230 ± 10 nm	C: 57 ± 1 nm S: 58 ± 2 nm	C: 15 ± 0.5 nm S: 15 ± 0.5 nm
10V Anodized	C: 220 ± 5 nm S: 230 ± 10 nm	C: 58 ± 1 nm S: 63 ± 2 nm	C: 15 ± 0.5 nm S: 15 ± 0.5 nm
20V Substrate	C: 215 ± 5 nm S: 230 ± 10 nm	C: 55 ± 1 nm S: 58 ± 1 nm	C: 15 ± 0.5 nm S: 15 ± 0.5 nm
20V Anodized	C: 220 ± 5 nm S: 230 ± 10 nm	C:133 ± 1 nm S: 136 ± 6 nm	C: 19 ± 0.5 nm S: 19 ± 1 nm
90V Substrate	C: 210 ± 5 nm S: 230 ± 10 nm	C: 58 ± 2 nm S: 59 ± 2 nm	C: 15 ± 0.5 nm S: 15 ± 0.5 nm
90V Anodized	C: 235 ± 5 nm S: 260 ± 10 nm	C: 131 ± 2 nm S: 130 ± 6 nm	C: 48 ± 1 nm S: 48 ± 1 nm

Regardless of the initial surface roughness, anodizing at 10 V doesn't change the roughness of the sample. In the case of the anodizing at 20 V, the roughness of the anodized samples depends on two different contributions, the roughness of the substrate R_S and the roughness induced by the reaction of oxidation R_{OX}. The R_{OX} contribution seems to be negligible in regard of R_S contribution for the P300 series, moderate (an increase of 30%) for the Vibrometer series and significant (increase of 150%) for the Alumina series.

It important to notice that the time needed to reach the maximum anodizing potential is a few seconds when anodizing at 10 V or 20 V whereas it is nearly thirty seconds when anodizing at 90V. The R_{OX} contribution was expected to be greater for longer anodizing times. For the 90 V vibrometer sample the influence of the oxidation reaction on the roughness is preponderant and corresponds to an increase higher than 200% of the initial value. The R_{OX} contribution is also noticeable in the case of the P300 series even if its effect is less remarkable (around 10%). The value of the roughness of the samples of the Alumina series didn't change after anodizing when the potential was changed from 20 V to 90V.

When the anodizing potential is low, the surface topology remains the same and when a certain potential threshold is reached, the surface topology is changed during the oxidation reaction. This potential threshold seems to be influenced by the roughness of the substrate: the threshold is low when the roughness is high (P300) or small (Vibrometer) and seems to be high for intermediate values of the roughness (Alumina). However more experiments are needed to confirm these observations such as adding intermediate and higher values of the potential or intermediate roughness values.

III – B] Optical characterizations

Optical characterizations of the samples were performed on Optimines, a goniospectrophotomoter developed by our research team [12]. These characterizations consist in measuring the BRDF (Bidirectional Reflectance Distribution Function) of the samples. The experimental BRDF is defined by the equation (1):

$$\text{BRDF}\ (\theta i,\varphi i,\theta r,\varphi r,\lambda) = \frac{F_r\,(\lambda,\theta_r,\varphi_r)}{F_{direct}(\lambda,\theta_i,\varphi_i)\times\Omega_s\times\cos(\theta_i)}\quad , \qquad (1)$$

where F_r is the reflected light flux for each detection direction (θ_r,φ_r), F_{direct} is the measured flux when the source is striking directly the detector, Ω_s is the source solid angle (12.10^{-6} sr).

BRDF measurements were converted into reflectance spectra by using the equation (2):

$$\rho(\theta i,\varphi i,\theta r,\varphi r,\lambda) = \text{BRDF}\ (\theta i,\varphi i,\theta r,\varphi r,\lambda) * \Omega_s * \cos\,(\theta i)\ , \qquad (2)$$

where ρ is the reflectance of the sample. Note that this reflectance corresponds to the Fresnel coefficient for the Vibrometer and Alumina sample series as the angular variations of the signal measured by the goniometer are limited by the goniometer angular resolution. This is not the case for P300 sample series.

The measurements were performed in a specular condition with an angle of incidence of 45°. Due to a big difference in the reflectance values, reflectance spectra of the samples of the Alumina and Vibrometer series are represented together for each potential on top of the figure 1 and all the P300 samples are represented on the bottom of the figure 1.

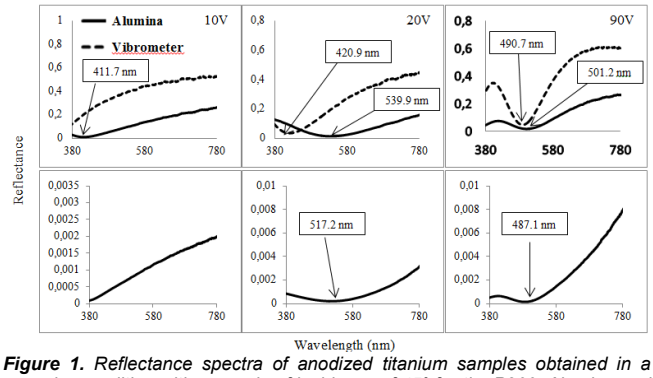


Figure 1. *Reflectance spectra of anodized titanium samples obtained in a specular condition with an angle of incidence of 45° for the P300, Alumina and Vibrometer series and for the 10V, 20V and 90V anodizing potentials.The arrows indicate the local minimum of the spectra.*

III – C] Visual characterizations

All the three samples anodized at 90 V exhibit almost the same color (see Figure 2). A slight hue difference is observed for the Alumina sample. The local minimum of the Vibrometer and P300 reflectance spectra are reached for the same wavelengths whereas it is slightly shifted towards the "red" wavelengths for the Alumina sample.

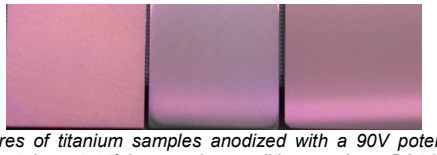


Figure 2. *Pictures of titanium samples anodized with a 90V potential. The picture has been taken at 45° in specular conditions under a D65 illuminant. From the left to the right: P300, Alumina and Vibrometer series.*

In the case of the samples anodized at 20 V, the color of the sample from the Vibrometer series is completely different from the color of the samples from the two other series as shown on the Figure 3. The shape of the reflectance spectra are almost the same for the Alumina and P300 series; but the shape of the reflectance spectrum of the Vibrometer series is different (different value of the local minium). This sample is also non gonioapparent contrary to the P300 and Alumina samples.

Figure 3*. Pictures of titanium samples anodized with a 20V potential. The picture has been taken at 45° in specular conditions under a D65 illuminant. From the left to the right: P300, Alumina and Vibrometer series.*

In the case of the samples anodized at 10 V, the local minimum is reached for wavelengths out of the visible range for the samples from the P300 and Vibrometer series (respectively 369 and 360 nm). The shape of the reflectance spectrum from those two series is different in the visible range and it explains their different colors as shown on the figure 4. The color of the Vibrometer series is totally desaturated (gray color). The reflectance spectrum of the sample of the Alumina series has a minimum in the visible range (412 nm) and the sample exhibits a saturated yellow color.

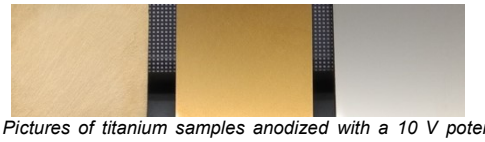


Figure 4*. Pictures of titanium samples anodized with a 10 V potential. The picture has been taken at 45° in specular conditions under a D65 illuminant. From the left to the right P300, Alumina and Vibrometer series.*

This study shows that the sample roughness plays a huge role in the sample color and that it can also change the gonioapparence for a given anodizing potential. Some further studies are nevertheless required to better understand how the roughness modifies the color and the gonioapparent behavior of anodized titanium samples. The modification of the color properties of the samples for a given anodizing potential could be due to differences between the average oxide layer thicknesses. The roughness would thus influence the oxide growth during the anodizing process. These modifications could also be due to the influence of the microfacets at the sample surface on the way the sample reflects light, modifying the perceived color of the sample.

III – D] Ellipsometric characterizations of mirror polished samples

Ellipsometric measurements have been carried out by a phase modulation ellipsometer, Horiba Jobin Yvon UVISEL® on the Alumina and Vibrometer series. The P300 series couldn't be measured efficiently by ellipsometry due to its too high roughness.

Ellipsometry techniques are described in details in reference [13]. To describe the spectral behavior of the refractive index, two dispersion laws were used:

-the classical dispersion model is based on the Lorentz classical theory (1878) of interaction between light and matter. This law is used for the titanium substrate.

-the new amorphous dispersion model is an optimized model to obtain extinction coefficient and refractive index. It is derived

from the Forouhi-Bloomer formulation. It is used for amorphous TiO_2 layer.

The anodized titanium sample is represented as a four layer surface in the ellipsometric modeling, as described in the figure 5. The first layer is the titanium substrate supposed to have an infinite thickness. The second layer is the interface between the titanium substrate and the titanium oxide layer and is noted as L1. This layer represents the surface roughness of the substrate and is considered as a mixed material composed of 50% Ti and 50% TiO_2. The third layer is the oxide layer noted as L2. The fourth layer noted as L3 corresponds to the interface between the oxide layer and the air. It is modeled as a mixed material composed of air (50%) and TiO2 (50%) also in order to simulate the oxide layer roughness.

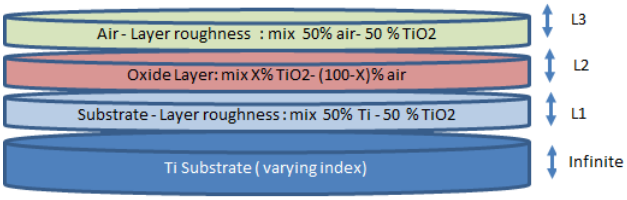


***Figure 5**. Representation of the four layer ellipsometric model.*

Ellipsometric measurements were performed on all samples at three different angles, 65°-70°-75°. It is important to notice that all the models were adjusted at the same time; the optimization takes into account the 6 samples for the three angles (18 parameters). The substrate is considered the same for all samples and its refractive index is adjusted during the modeling (the starting refractive index is coming from the database of the ellipsometer software). The TiO_2 material is considered the same for all the samples. When the refractive index value drops in the layer L2, the model supposes that pores are present in this layer. This porosity is noted as the factor X, considered as air in the model. It is important to note that this porosity is variable for all the samples. The thickness of the different layers (see table 2), the refractive index of the titanium and the titanium dioxide layer were estimated with this model.

Table2: Thicknesses and oxide layer porosity factor X estimated by ellipsometric measurements.

	L1 (nm)	L2 (nm)	L3 (nm)	X (%)
Alumina 10V	3.4	26.9	2.2	0
Alumina 20V	10.8	41.1	3.2	0
Alumina 90V	38.8	171.5	8.6	12.7
Vibrometer 10V	2.7	11.2	6.2	0
Vibrometer 20V	3.5	27.4	2.1	0
Vibrometer 90V	31.3	148	7.1	2.2

Only the oxide layer of the samples anodized at 90V are found to beporous. In the case of the sample of the Vibrometer series, the pores seem to be small in both number and size but this observation needs to be confirmed by SEM (Scaning Electron Microscopy) imaging for example.

IV – Optical modeling

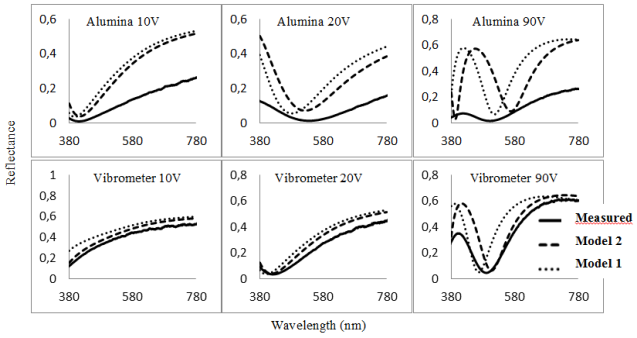
IV – A] Abeles modeling based on ellipsometric measurements

To model the specular reflectance of an anodized titanium sample, an Abeles matrix formalism was used. It is based on the transfer-matrix method used to analyze the propagation of electromagnetic waves through a layered medium [14].

The medium is supposed to be composed of a bulk homogeneous TiO_2 layer and an infinite Ti substrate. Both interfaces are plane and parallel. The Ti and TiO_2 refractive indexes and the TiO_2 layer thickness obtained through ellipsometric measurements were used as parameters for the model. During this study, the angle of the incident light is fixed at 45° and the reflectance spectra were compared to the results presented before (see part III-B).

Two different types of models are presented in figure 7. The first one (denoted as model 1 on the figure 7) considers an oxide layer thickness equal to the L2 value of the ellipsometric measurements. The second one (denoted as model 2 on the figure 6) considers an oxide layer thickness equal to L2+(L1+L3)/2.

Both models are overestimating the value of the reflectance for all the potentials and for all the surface finishing. The results are in a better agreement for the Vibrometer series than for the Alumina series. The number of extrema and their positions are in quite good agreement between the model and the measurements, as well as the global shape of the spectra. Except for 90V samples the second model seems to retrieve more accurately the positions of the extrema of the spectra. For the 90V Vibrometer sample the second model overestimates the positions of the extrema whereas the first model underestimates them. For the 90 V Alumina sample both models overestimate the positions of the extrema, but the first model gives values closer to the measured spectrum.



	10V meas	10V model 1	10V model 2
Alumina	417,7 nm	397,6 nm	414,4 nm
Vibrometer	/	/	/
	20V meas	**20V model 1**	**20V model 2**
Alumina	539,9 nm	481,6 nm	522,4 nm
Vibrometer	420,9 nm	400,8 nm	417,6 nm
	90V meas	**90V model 1**	**90V model 2**
Alumina	501,2 nm	516 nm	568 nm
Vibrometer	490,7 nm	466,4 nm	506,4 nm

***Figure 6.** Comparison between an Abeles reflectance model using the material parameters obtained through ellipsometric measurements and goniospectrophotometric measurements for Alumina and Vibrometer series for the three potentials 10, 20 and 90V. The table below indicates the positions of the local minimum for each curve of the top graphs.*

Some improvements of the optical model are planned as for example using the same 4 layer model as this used in the ellipsometric measurements including mixed air-Ti and air-TiO_2 materials. It can be noticed that some improvements of the

ellipsometric model are also in discussion. The model could include roughness measurements or experimental reflectance spectra to optimize the given results. Comparisons between the thickness measurements obtained by ellipsometry and thickness measurements obtained by another technique such as X-Ray reflectometry are also planned.

IV – B] First step of roughness modeling: varying thickness

Based on the Abeles matrices, we developed a model where the roughness of the sample is represented as a thickness variation around an average thickness value. The rough sample is decomposed into a sum of perfectly plane samples with thickness values taken in the interval [Value without roughness – $R_{vp}/2$; Value without roughness + $R_{vp}/2$] with a uniform distribution, where the roughness parameter R_{vp} is the maximum peak-to-valley height.

The reflectance spectrum obtained during a spectrophotometric measurement is the macroscopic response that takes into account all the local contributions coming from the variations of thickness present on the surface of the sample. To include this effect into the model, the interval of thickness values is divided into small increments corresponding to the contribution of the local thickness values. For each increment, a reflectance spectrum is computed. To obtain the global response of the material, a non-weighted arithmetic average of all the reflectance spectra is made. As an example, a sample with an oxide layer of 170 nm and a total thickness variation of 10 nm with thickness increments of 1 nm is showed on the figure 7. Note that this model corresponds to a sample with a roughness parameter R_a equal to 2.7 nm (as all the thickness values are assumed to have the same weight).

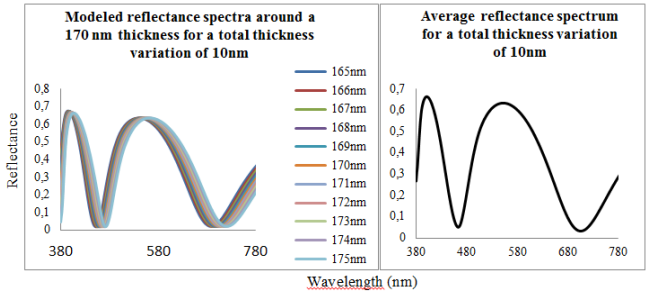


Figure 7. *Modeled reflectance spectrum of a sample with an oxide layer thickness of 170 nm and a total thickness variation of 10 nm. On the left are represented the reflectance spectra of the local contributions with an increment of thickness of 1nm around a thickness value of 170 nm. On the right is represented the arithmetic average of all the local contributions. This model corresponds to a sample with a roughness parameter R_a equal to 2.7 nm.*

The same process has been applied to 50 nm and 100 nm total thickness variations with 5 and 10 nm increments (respectively R_a=13.6 nm and 27.3 nm). The average reflectance spectra have been converted into colors components and represented on the CIE-xy chromaticity diagram on figure 8.

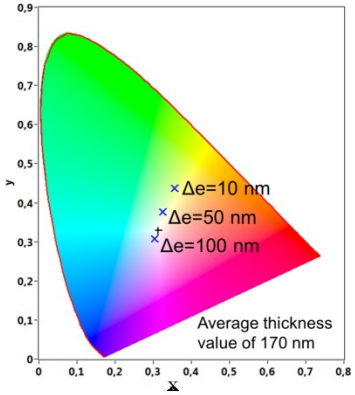


Figure 8. CIE*-xy chromaticity diagram representing the colors of three samples with a 170 nm oxide layer thickness and total thickness variations ranging from 10 to 100 nm.*

We observe that the rougher the sample is the less saturated its color is. Also roughness variations seem to change only the saturation of the color and not its hue. This model nevertheless still needs to be confronted to measured data. Further improvements of this model could be the use of a thickness distribution extracted from the profilometric measurements of the samples.

V – Design of an experimental setup to perform perception tests: the Goniobox

An experimental setup was designed and built to perform perception tests of the gonioapparence of the samples. To be able to compare the perception tests to standard color measurements, the experiment has been designed to offer the same geometries of illumination and observation as the most common multi-angle spectrophotometers. First perception tests will consist in asking the observer to indicate the angular values where color changes of the sample are perceived. A referenced color map will also be used in conjunction with the box to help the observer describing the different colors of the samples. The Goniobox is described on the figure 9.

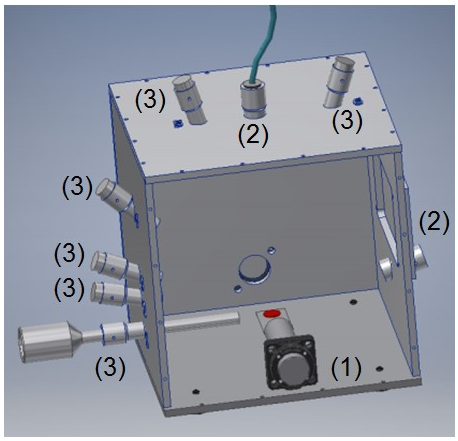


Figure 9. *Descriptive diagram of the Goniobox. (1) a rotating sample holder, (2) Light source holes and (3) observation holes and tube.*

The Goniobox consists of two illumination and six observations holes, a rotating sample holder and an observation

tube. Those holes enable to observe the samples in various conditions:

-in specular conditions for 15°, 20°, 45°, 65°, 75° (using the rotation of the sample with the 0° illumination hole).

-in various non-specular conditions for an illumination angle of 45° (45°/-65°, 45°/-30°, 45°/0°, 45°/20°, 45°/30°) and some other configurations with 0° and 15° illumination angles.

The observation tube is graduated and used to observe the sample at the same distance regardless of the angle used. The lighting source is a D65 illuminant projected into the box through a collimated optical fiber.

Some improvements are needed, to optimize the illumination system to obtain a good lighting, both in terms of homogeneity and irradiance, of the sample surface, while avoiding the potential inconvenience to the user of a too high irradiance.

VI – Conclusion and perspectives

Surface roughness plays a key role in the color and the gonioapparent property of anodized titanium. Roughness measurements of the titanium substrate and the oxide layer surface showed that both the substrate roughness and the anodizing process influence the surface roughness of anodized titanium. Further investigations need nevertheless to be carried out to understand the way roughness influences color.

Samples have been characterized by ellipsometry. These parameters have been put into an Abeles based optical model in order to simulate the optical properties of the material. The model is overestimating the value of the reflectance but the number of extrema and their positions are in quite good agreement between the model and the measurements, as well as the global shape of the spectra. Improvements of both the optical model and the ellipsometric model used to extract the material parameters can be performed. The ellipsometric model could include roughness measurements or experimental reflectance spectra to optimize the given results. X-Ray reflectometry could also be performed to give another assessment of the oxide layer thickness.

To give first clues about the way roughness may influence color, a first model where the roughness of the sample is described as local variations of the oxide layer thickness has been presented. This model shows that a rougher sample exhibits a less saturated color. Nevertheless this model still needs to be confronted to measured data and could be improved by using a thickness distribution extracted from the profilometric measurements.

An experimental setup suited to perform perception tests of gonioapparent samples has also been built, allowing to observe the samples on the same geometries as common commercial multi-angle spectrometers. It could provide a future point of comparison between measured and perceived colors of gonioapparent samples.

This work was supported by the LABEX MANUTECH-SISE (ANR-10-LABX-0075) of Université de Lyon, within the program "Investissements d'Avenir" (ANR-11-IDEX-0007) operated by the French National Research Agency (ANR).

References

[1] Carp O, Huisman CL, Reller A. "Photoinduced reactivity of titanium dioxide", Prog Solid State Chem, vol 32 (1-2), p 32-177, 2004

[2] Nakajima A, Koizumi S, Watanabe T, Hashimoto K. "Effect of repeated photo-illumination on the wettability conversion of titanium dioxide", J Photochem Photobiol A Chem, vol. 146, no. 1-2, p 129-132, 2001

[3] Lynne Bartlett, "An unusual phenomenon observed when anodising CP titanium to produce coloured surfaces for jewellery and other decorative uses", Optics & Laser Technology, vol. 38, no. 4–6, pp. 203-486, 2006

[4] Pérez Del Pino A, Serra P, Morenza J.L, "Coloring of titanium by pulsed laser processing in air," Thin Solid Films, vol. 415, no. 1–2, pp. 201–205, 2002.

[5] Diamanti, M. V, Pedeferri, M. P, "Effect of anodic oxidation parameters on the titanium oxides formation", Corrosion Science, vol. 49, no. 2, p 939–948, 2007

[6] Cheng S, Wei D, Zhou Y, "Formation and structure of sphene/titania composite coatings on titanium formed by a hybrid technique of microarc oxidation and heat-treatment", Applied Surface Science, vol. 257, no. 8, pp. 3404–3411, 2011

[7] Van Gils S, Mast P, Stijns E, Terryn H, "Colour properties of barrier anodic oxide films on aluminium and titanium studied with total reflectance and spectroscopic ellipsometry," Surf. Coatings Technol., vol. 185, no. 2–3, pp. 303–310, 2004.

[8] Diamanti MV, Del Curto B, Ormellese M, Pedeferri MP, "Photoactive and colored anodic oxides on titanium for architectural and design applications", Clean Technol, vol. 1, pp. 170-173, 2008

[9] Charrière R, Lacaille G, Pedeferri MP, Faucheu J, Delafosse D, "Characterization of the Gonioapparent Character of Colored Anodized Titanium Surfaces", Color Research & Application, vol.40, no. 5, pp. 483-490, 2014

[10] Diamanti, M. V, Spreafico, F. C, Pedeferri, M. P, "Production of Anodic TiO2 Nanofilms and their Characterization", Physics Procedia, vol. 40, pp. 30–37, 2013

[11] Lamolle S. F, Monjo M, Rubert M, Haugen H. J, Lyngstadaas S. P, Ellingsen J.E, "The effect of hydrofluoric acid treatment of titanium surface on nanostructural and chemical changes and the growth of MC3T3-E1 cells", Biotmaterials, vol. 30, no. 5, 2009

[12] Matsapey N, Faucheu J, Flury M, Delafosse D, "Design of a gonio-spectro-photometer for optical characterization of gonio-apparent materials", Measur. Sci. Tehcnol, vol. 24, no. 6, 2013

[13] Azzam R. M. A, Bashara N. M, Ellipsometry and polarized light, North Holland, 1987.

[14] F. Abeles, Le Journal de Physique et le Radium, "La théorie générale des couches minces", vol.11, pp.307–310, 1950

Author Biography

Quentin Cridling received his Master degree in Materials Sciences for Structures and Energy from the INSTN CEA Saclay (2013). He is doing his PhD under joint supervision of the Ecole des mines de Saint-Etienne (France) and the Politechnico di Milano (Italy) since 2014. His PhD work is focused on the parameters influencing on the gonioapparence of anodized titanium.