Color variation of TiO_2/Ti samples under wear tests

Sarah MARION[1,2], Matthieu LENCI[1], Clotilde MINFRAY[2], Vincent FRIDRICI[2], Laurent DUBOST[3], Jenny FAUCHEU[1], Renée CHARRIERE[1]

[1] Mines Saint-Etienne, Université de Lyon, CNRS, UMR 5307 LGF, Centre SMS, F-42023 Saint-Etienne France

[2] Laboratoire de Tribologie et Dynamique des Systèmes, UMR CNRS 5513 ECL ENTPE, Université de Lyon, Ecole Centrale de Lyon, F-69134 Ecully cedex

[3] IREIS, ZI Sud-Avenue Benoît Fourneyron, F-42160 Andrézieux-Bouthéon

Although titanium is not a noble material, it is attracting more and more attention in the luxury industry [1,2] (jewelry, watches, packaging) because of its lightness, hypoallergenic properties and, above all, the many colors it can produce when coated with a thin layer of TiO_2. However, its use in luxury goods is currently limited because its colors do not last very long. The wear resistance of thin colored layers of TiO_2, and especially the preservation of the original color, is an important issue for luxury jewelry. The interferential origin [3] of the color makes it particularly sensitive to a variation in thickness, but also to a variation in the chemical composition and internal structure of the oxide layer through a change in the refractive index.

Mirror polished TiO_2/Ti samples were obtained either through an anodizing process in galvanostatic mode or by magnetron sputtering. The oxide layer thickness is about 120 nm for the anodized samples and 140 nm for the sputtered ones, which corresponds respectively to yellow and purple colored samples. Ball-on-flat dry or wet (with artificial sweat) tribological tests were then conducted on these samples, changing their color (see **Figure 1** a) and b)). To understand these color variations, X-Ray Photoeletron Spectroscopy (XPS) analyses conducted inside and outside the wear mark. They show neither a stoichiometric modification of the oxide nor a chemical composition modification. Local reflectance spectra measurements performed inside the wear marks show that these variations can be explained by a reduction of the oxide layer thickness.

A more detailed analysis of the color variations inside the wear marks for the anodized sample (see **Figure 1** a)) shows local color variations with dark blue spots inside the light blue wear mark. To go further in the analysis of these color variations, characterizations of the initial color of the material have been performed at a microscopic scale. Microscopic images show that the samples exhibit blue and yellow areas (see inserts of **Figure 1** c) and d)). Through Electron Backscatter Diffraction (EBSD) analyses of the titanium substrate crystallographic orientation, blue areas were correlated with orientations of the titanium α-phase close to the basal plane (0001), whereas yellow areas were correlated to other orientations of the α-phase and the β-phase. A Focused Ion Beam (FIB) cut lamella were taken at the intersection of a blue and a yellow area (see **Figure 1** c)). It can be seen that the blue area corresponds to a porous oxide layer, whereas the oxide is dense for the yellow one.

To understand how this porosity difference can influence the tribological behavior of the material, nano-tribological tests were conducted under an Atomic Force Microscope (AFM) in contact mode inside a yellow and a blue area. It can be seen (**Figure 1** d)) that for the same number of wear cycles, the height variation of the sample surface is more important on the blue area than on the yellow one. This is correlated with the fact that the oxide layer is porous on blue areas and dense on yellow ones. This difference is wear resistance properties of blue and yellow areas could explain the non-uniformity of the wear trace in **Figure 1** a), with the presence of the dark blue spots, corresponding to a thinner oxide layer thickness.

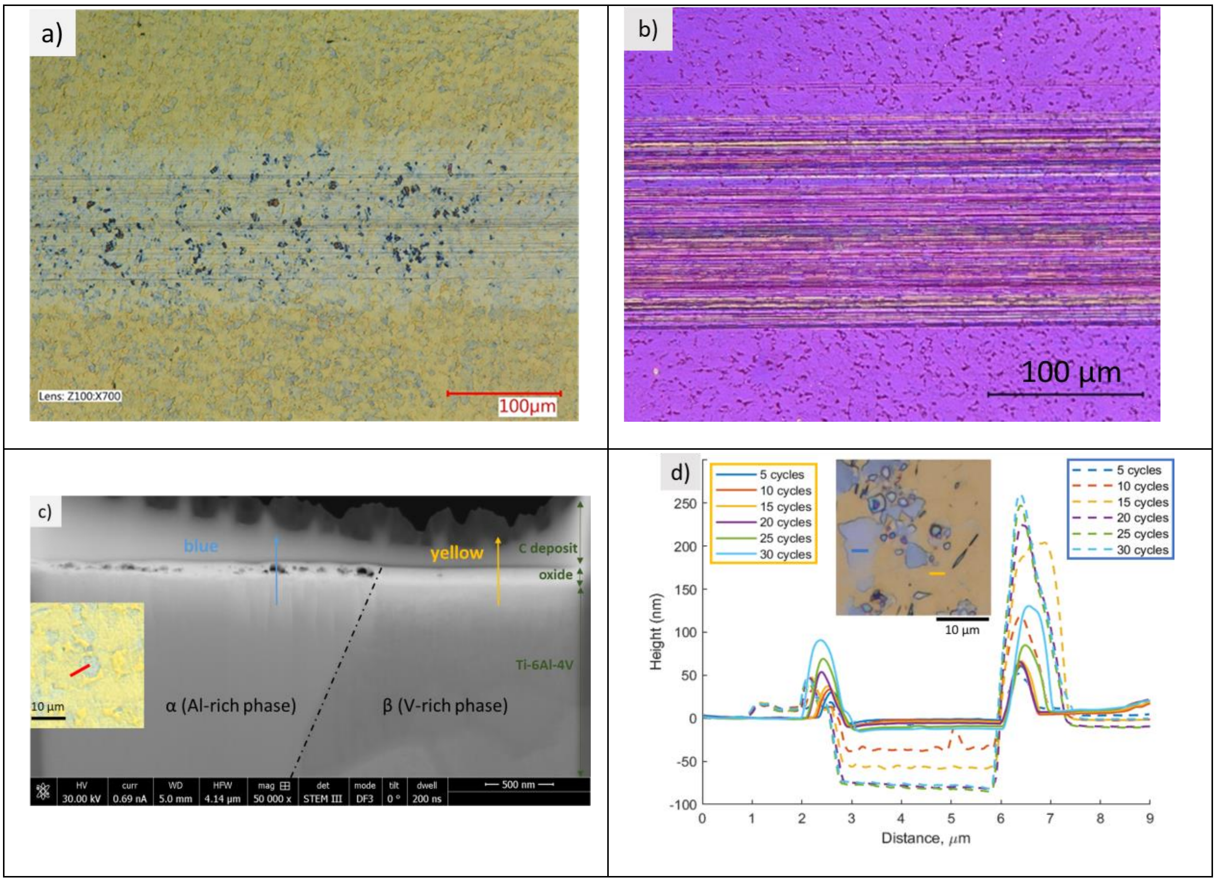

Figure 1 a) Wear mark of a 10 cycles dry tribological test on an anodized TiO_2/Ti sample. b) Wear mark of a 10 cycles tribological test under artificial sweat on a sputtered TiO_2/Ti sample. c) STEM image of a FIB cut lamellae taken at the intersection of a blue and a yellow area. The insert is a microscope image showing with a red line the area were the FIB lamellae were cut. d) Depth analysis of nano-tribological tests conducted under AFM in a yellow area (plain curves) and in a blue area (dashed curves). The insert is a microscopic image of the sample showing with a blue and a yellow line the areas were the nano-tribological tests were conducted.

References :

[1] L. Bartlett, Opt. Laser Technol. **38**, 440–444 (2006).

[2] M. V. Diamanti, B. Del Curto, V. Masconale, C. Passaro, and M. P. Pedeferri, Color Res. Appl. **37**, 384–390 (2012).

[3] M. V. Diamanti, B. Del Curto, and M. Pedeferri, Color Res. Appl. **33**, 221–228 (2008).

Mots clés : colored titanium alloy, anodizing, magnetron sputtering, wear tests, color durability