Highlighting of a crystalline and amorphous TiO_2 bilayer by Transmission Electron Microscope investigations: conventional TEM coupled with EDX and ASTAR mappings

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1. INTRODUCTION

TiO_2 has been deposited on TiNi superelastic substrate in order to prevent any Ni diffusion for its further potential use in orthodontics. TiO_2 has been synthetized by a sol-gel technique; then a thermal treatment has been applied in order to partially crystallize the thin film. The objective of this work is to put in evidence if the TiO_2 film contains amorphous and crystalline parts. For this purpose, the material has been characterized by TEM microscopy on a transversal cross-section thin lamella priory prepared by double column FIB-SEM microscopy.

2. RESULTS

2.1 Chemical mappings

EDX mappings show that the TiO_2 layer is ~100 nm thick with two layers: a denser part near the substrate and a superior part that appears to be porous (see Fig. 1). This porosity can be easily explained by the sol-gel growth method. It should also be noted that some Ni has diffused through the TiO_2 layer (see Fig. 1d)). Because of its biocompatibility TiO_2 is chosen as a protective coating in order to prevent contact with Ni (coming from the substrate).

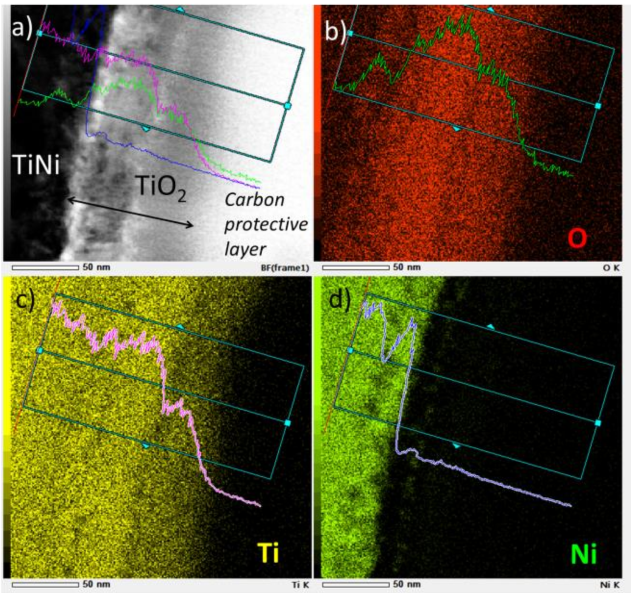

Figure 1. a) Bright-field STEM image of the TiNi substrate /*crystalline and amorphous* TiO_2 / C protective layer stacking.
EDX elemental mappings b) O-K c) Ti-K d) Ni-K.
The intensity of each ray, integrated on the selected area, is superimposed on each image.

2.2 Precession-assisted diffraction spot recognition

The precession assisted crystal orientation mapping technique, ASTAR, which is a TEM-based diffraction spot recognition technique [1] has been used to acquire orientation and phase maps of the TiO_2 deposited on TiNi substrate. Orientation and phase mappings (see Fig. 2 and 3) put in evidence that the dense part near the substrate is crystalline; with both anatase and rutile structures and that the grains are very small (with a size of about 10 to 50 nm).

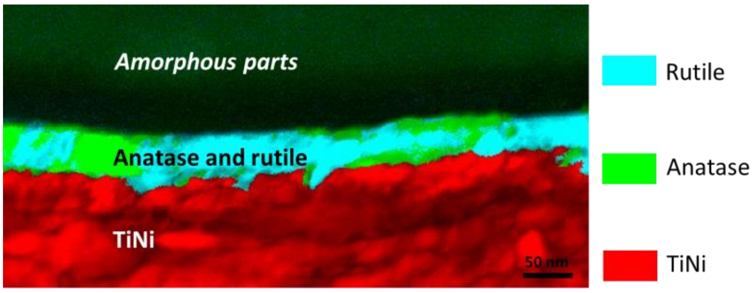

Figure 2. Phase combined to correlation index map on the TiNi/ TiO_2/ C -protective layer- stacking

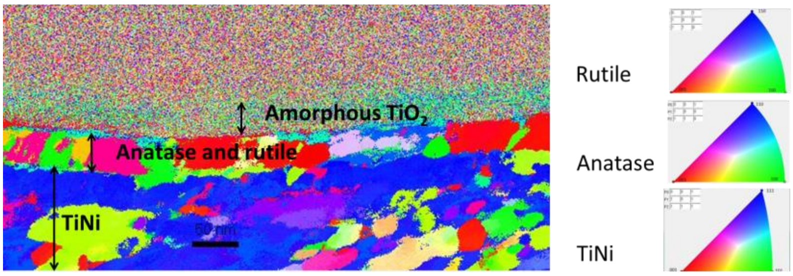

Figure 3. ASTAR orientation on the TiNi/ TiO_2/ C -protective layer- stacking.

The Virtual Dark-Field (VDF) images -reconstructed from electron diffraction patterns- permits to highlight the amorphous TiO_2 layer. The amorphous TiO_2 material generates diffuse rings in the diffraction patterns that are detected using a ring type virtual aperture [2]. In VDF image, the amorphous TiO_2 part appears in white whereas the other materials appear darker (see Fig. 4a)). If the small ring of the amorphous TiO_2 material is selected (instead of the larger one); the amorphous and crystalline parts TiO_2 are very well highlighted (see Fig 4b)).

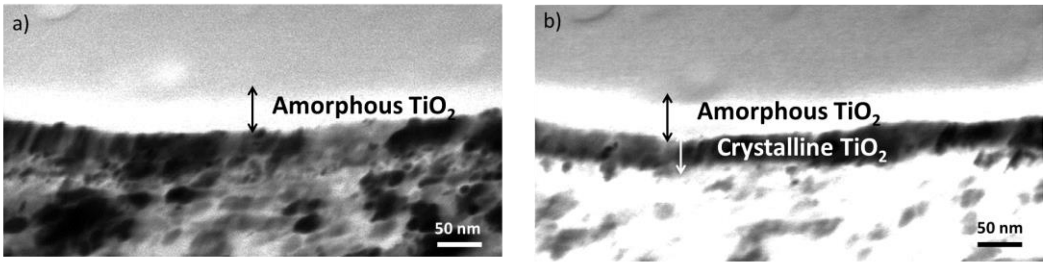

Figure 4. Virtual Dark-Field images that highlights the amorphous TiO_2 layer ; a) the large ring in the diffusion pattern of the TiO_2 material is selected, b) the small ring in the diffusion pattern of the amorphous TiO_2 material is selected.

3. CONCLUSION

The identification of the crystalline and amorphous TiO_2 bilayer has been based on EDX, ASTAR mappings together with TEM observations (see Fig 5.). The TiO_2 thin film is indeed composed of a crystalline layer, located towards the substrate ~50 nm thick, and of an amorphous and porous superior layer ~50 nm thick. The crystalline TiO_2 layer presents both anatase and rutile structure with very small grains. This peculiar microstructure, both crystalline and amorphous, permits to optimize the mechanical properties of the thin film.

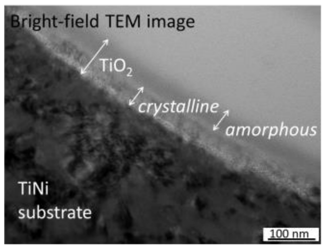

Figure 5. Bright-field TEM image

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[1] Rauch E.F. and Véron M., *Automated crystal orientation and phase mapping in TEM*, Mater. Charact., **98**, (2014), 1-9.

[2] Rauch E.F. and Véron M., *Virtual dark-field images reconstructed from electron diffraction patterns*, Eur. Phys. J. Appl. Phys., **66**, (2014), 10701-1-5