

## ***In Vitro* Behavior and Surface Morphology of Modified 316L Stainless Steel Stents**

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When compared with conventional bare metal stents, such as 316L stainless steel, the introduction of drug-eluting stents can promote reduction in the incidence of in-stent restenosis[1]. However, the chemical discrepancy between the metallic stent and the polymeric material that acts as the reservoir for the drug is responsible for some problems during the cardiovascular surgery. Besides the research work aiming at the development of new bulk alloys for stent production, focus as been also directed to the surface modification of these devices[2,3]. However, the use of functional graded coatings (FGC), i. e., coatings with a gradient of chemical composition between the substrate and the outmost layer, has never been reported in devices for cardiovascular surgery.

In this work, sputtering from 316L stainless steel and poly(tetrafluoroethylene) (PTFE) targets was used to uniformly modify the surface of 316L stainless steel (Fig.1) aiming at the creation of a continuum in chemical composition. The variation of the PTFE discharge power resulted in several coatings (thickness from 400 to 700 nm) with fluorine contents up to 60at%. The results from XPS (X-ray Photon Spectroscopy), EPMA (Electron probe Micro Analysis) SEM (Scanning Electron Microscopy), TEM (Transmission Electron microscopy) and cell culture are discussed in this work.

The chemical gradient was confirmed by XPS as illustrated in figure 2 for fluorine. The SEM surface morphology analysis reveals island-like features for thin films with higher fluorine concentrations (40-60at%) (Fig.3). An EPMA elemental map distribution elucidated the fact that “islands” correspond to high fluorine concentrations (Fig.3) while the remaining surface is enriched in carbon (Fig.3). The microstructure of the deposited thin films changes with fluorine content. For lower F concentrations an fcc structure; for medium values amorphous, and for the 40-60at% range a composite structure. For the latest contents, a new ceramic phase ( $\text{FeF}_2$ ) acts a reinforcing material of the stainless steel matrix (Fig.4).

Considering the principal purpose of this work, the best results for the modification of stents were obtained for average fluorine concentrations of 10 at% where endothelial cell proliferation and morphology indicate improved biocompatibility of the modified surface (Fig.5 and 6). For the surfaces with 40 – 60at% fluorine attention must be paid to the fact that the release of high concentration of this ion, in a very short period of time, implicates a citotoxic effect on this cell line (Fig.5and 6).

### References

- [1] – J. Hausleiter et al., Eur. Heart J. 26 (2006) 1475.
- [2] – S. Choudhary et al., Int. J. Nanomed. 1 (2006) 41.
- [3] – F. J. Jing et al., J. Vac. Sci. Technol. A 24 (2006) 1790.

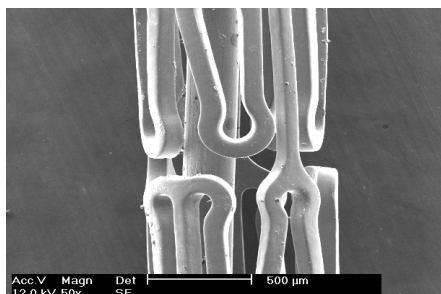


Fig.1. SEM image of a stainless steel stent before expansion (bar= 500  $\mu\text{m}$ ).

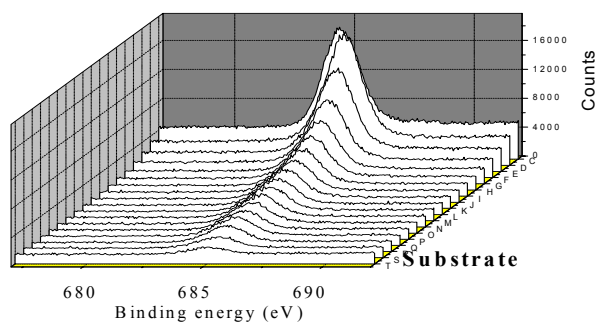


Fig.2. Fluorine discrete gradient evaluated by in-depth XPS ( $[\text{F}] \approx 10 \text{ at}\%$ ).

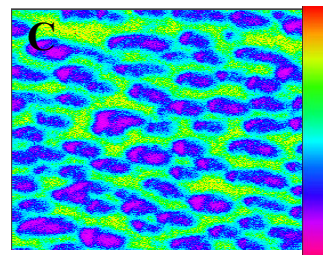
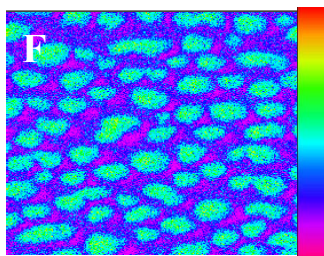
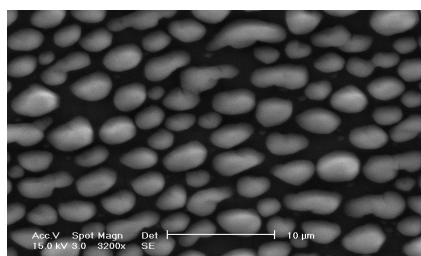


Fig.3. “Island-like” morphology (SEM) and fluorine (F) and carbon (C) elemental map distribution (EPMA) of thin film with 60at% fluorine (bar= 10  $\mu\text{m}$ ).

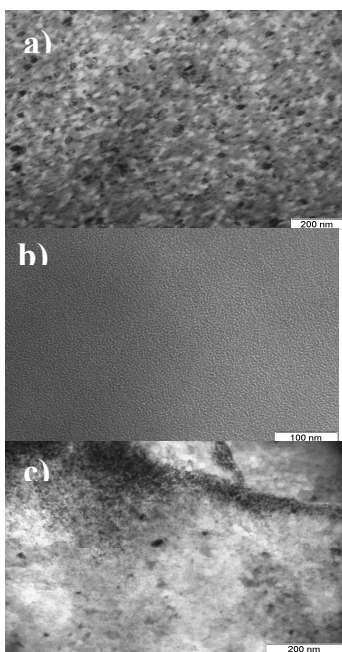


Fig.4. TEM images showing the evolution of microstructure with fluorine content: a)  $\text{F}=0 \text{ at}\%$  (bar=200nm); b)  $\text{F}=10 \text{ at}\%$  (bar=100nm); c)  $\text{F}=60 \text{ at}\%$  (bar=200nm).

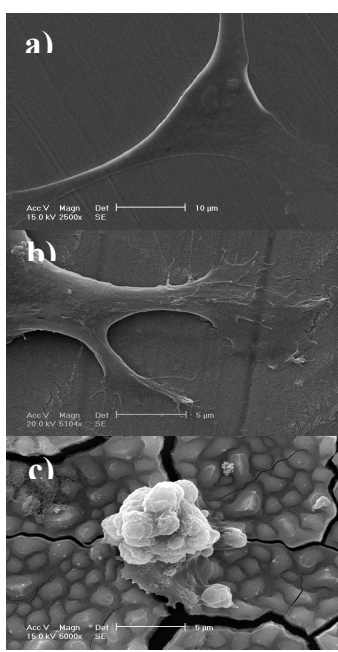


Fig.5. SEM micrographs of the endothelial cells after contact with several surfaces: a) 316L stainless steel (bar=10 $\mu\text{m}$ ); b)  $\text{F}=10 \text{ at}\%$  (bar=5 $\mu\text{m}$ ); c)  $\text{F}=60 \text{ at}\%$  (bar=5 $\mu\text{m}$ ).

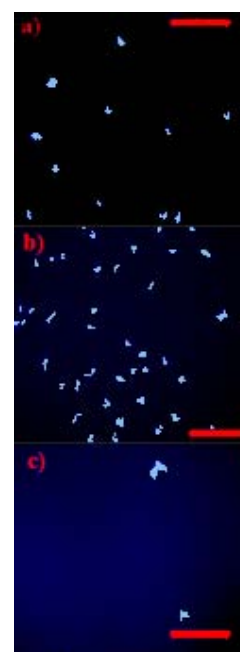


Fig.6. Endothelial cell proliferation assessed by nuclei fluorescence. a) 316L stainless steel; b)  $[\text{F}]=10 \text{ at}\%$ ; c)  $[\text{F}]=60 \text{ at}\%$  (bar = 100  $\mu\text{m}$ ).