PEEM/NEXAFS Analysis of Ultrathin Fluorocarbon Films for Coated Stents

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Introduction

Atherosclerosis will be a huge health issue over the next several decades, due to the increasing prevalence of heart disease in an aging population. This disease provokes a narrowing of the arteries and reduces blood flow. Coronary stents are implanted in the human body to provide a mechanical support to a diseased artery. Stents are a metallic scaffold most commonly made of 316L stainless steel. Restenosis was a major drawback with the first generation of bare metal stents. Therefore, coated and drug-eluting stents have been introduced in order to reduce the clinical complication rate. However, coating failures have still been reported mainly due to the plastic deformation that occurs during post-implantation stent expansion [1]. According to finite elements modeling, this plastic deformation could be up to 25% [2] and can produce surface defects that influence the adhesion and cohesion properties of the film. The development of durable, stable and adherent stent coatings are a major concern according to the U.S. Federal Drug Administration (FDA) [3]. However, no specific test procedures have been proposed. The use of high sensitive characterization techniques, such as synchrotron based PEEM and NEXAFS, could be useful to detect defects or film failures.

Science

Ultrathin fluorocarbon coatings deposited by radio-frequency plasma have been developed in our laboratory [4]. Plasma deposition is known to produce adherent and cohesive films. Fluorocarbon polymers have a well established biocompatibility and are chemically inert, highly hydrophobic, and are promising stent coatings considering their protein retention capabilities and thromboresistance properties [5]. The mechanical resistance of the film (to the plastic deformation occurring during in vivo insertion) as well as its chemical stability (in aqueous solution) are studied. Available techniques in our laboratory, such as X-ray Photoelectron Spectroscopy and High Resolution Electron Microscopy, have not shown any failure of the film after plastic deformation, such as cracks or delamination after mimicking stent expansion [4]. However, the ageing test in aqueous solution showed failure of the coating after several weeks of immersion.

Synchrotron X-PEEM and NEXAFS were expected to reveal the possible cause of the film failure during ageing in aqueous solution because of their high chemical sensitivity.

The aim of this work consists of investigating the adhesion and cohesion of a fluorocarbon coating deposited by pulsed RF-plasma on pre-treated 316L stainless steel. Flat coated samples were deformed at 25% in order to mimic a stent expansion [4]. Deformed and non-deformed samples with different coating thicknesses varying from 35 nm to 100 nanometres were analyzed to detect coating failures and chemical composition changes.

X-ray Photoelectron Spectroscopy (XPS – PHI 5600-ci spectrometer – Physical Electronics USA, Chanhassen, MN, USA), and X-ray Photoelectron Emission Microscopy (X-PEEM; CLS beamlines 10ID-1 and 11ID-1) were used to characterize the film homogeneity before and after plastic deformation.

Results and Discussion

XPS analyses of flat and deformed specimen showed continuous fluorocarbon films with no occurrence of any metallic compounds as shown in Figure 1 for the iron peaks (711 eV). In case of failure, such as delamination or cracks of the film, metallic compounds from the substrate should appear.

Specimens prepared in the same conditions were analyzed with the X-PEEM setting at the CLS in order to detect possible failures. Figure 2 shows the resulting NEXAFS fluorine and iron peaks for these specimens (35 and 100 nm, flat and deformed).

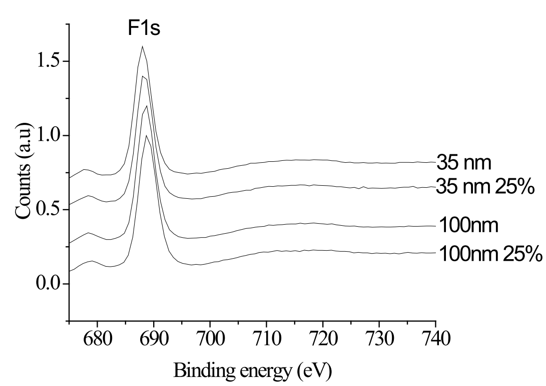

Figure 1: Fluorine and iron XPS peaks, for 35 and 100 nm flat and deformed specimens.

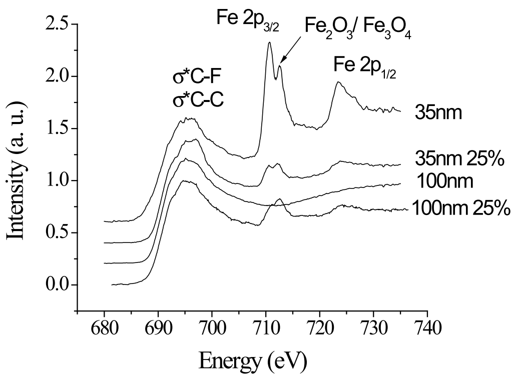

Figure 2: Fluorine and iron NEXAFS peaks (CLS) for 35 and 100 nm, flat and deformed specimens.

Iron peaks occur for all specimens, except for the flat 100 nm film. The detection of Cr and Fe at the surface of the non-deformed 35 nm coatings indicates the occurrence of porosity or nano-pinhole defects which were below the sensitivity of the XPS analyses. Unfortunately, the PEEM spatial resolution was not sufficient to image these alleged nano-defects as shown in Figure 3. The observed dark spots are related to topographic shadow effects due to slip bands and grain boundaries. The NEXAFS spectra of the deformed 100 nm coatings also revealed metallic peaks indicating stress induced cracking of those films. The X-PEEM/NEXAFS technique therefore permitted the detection of defects in the film continuity that were undetectable by the XPS technique.

Conclusion

The NEXAFS spectra did show the occurrence of metallic compound at the surface of the films, revealing the possible existence of nanopores or nanopinholes through the thinnest ones (35 nm) as well as deformation-induced cracking of the thickest ones (100 nm). These defects had eluded detection by XPS and SEM. The NEXAFS results were therefore essential in the determination of possible causes for the films' failure due to deformation and/or immersion in aqueous solution. This technique will also be useful for monitoring the progress of the optimization of the films as well as the film/metal interface. Pre- and post-treatments are currently being evaluated and will be validated with NEXAFS analyses.

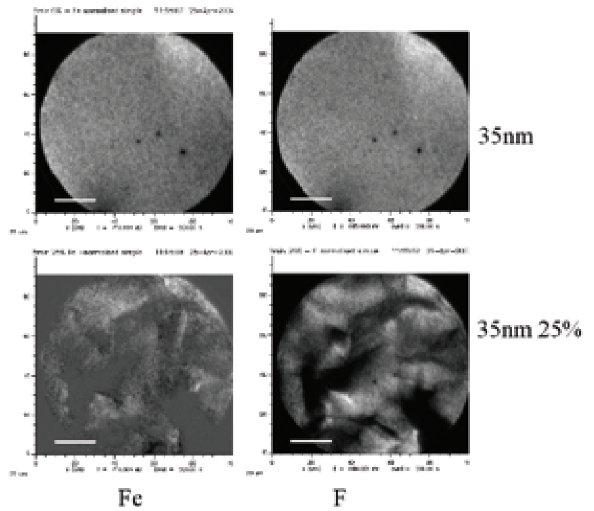

Figure 3: PEEM images of Fe and F elements for the 35 nm coating, before and after plastic deformation.

References

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