

Surface Fluorination with Argon Plasma Treatment
Sophie X Yang, Richard King, Lawrence Salvati, Ronald Konkle
DePuy Orthopaedics, Inc. Warsaw, IN 46581

Introduction:

It has been reported that fluoride ions can exchange with calcium ions in hydroxy-apatite crystals producing fluorapatite which has a higher lattice energy, increased crystallinity and better dissolution resistance than hydroxyapatite. As a result, it is believed that incorporating fluoride ions into the surface structures of orthopaedic implant materials may enhance bone on-growth. In the present study, CoCrMo implant materials were fluorinated using an energetic Ar plasma treatment process.

Methods:

For the present investigation, plasma fluorination treatments were conducted using 25mm diameter polished CoCrMo test coupons ($R_a = 0.01\mu\text{m}$). The plasma treatment process utilized a TePla 7200 Plasma Processing System (PVA TePla America, Inc. CA). Plasma treatments were conducted using Ar gas at a pressure of 300mTorr with a flow rate of 250 sccm. An $8 \times 12\text{cm}^2$ PTFE block (McMaster-Carr IL) was placed inside the plasma chamber as the fluoride source. The treatment time was kept constant at 10 minutes. The Rf power was set at 100, 500 or 1000 watts.

Following plasma treatment, the CoCrMo test coupons were transferred directly into the intro chamber of an X-ray Photoelectron Spectrometer (XPS) for surface characterization. The XPS system employed in this investigation was a PHI Quantera SXM system (Physical Electronics, Chanhassen, MN).

Results:

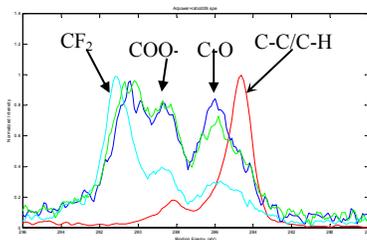


Figure 1, XPS C peaks on the CoCrMo surfaces before (red) and after 10 minutes of fluoridation treatment with different power: 100w (light blue), 500w (green) and 1000w (dark blue).

Figure 1 shows that C contamination peak was at 284.6eV before Ar plasma treatment. The 10-minute plasma treatment with a PTFE block eliminated C contamination and produced carbon-based groups, like CF_2 , COO^- and C-O on the metal surface. Among them, COO^- and C-O intensity increased with increasing the power, which showed that high power promotes polymer chain scission and oxidation during the plasma treatment.

Examination of the fluorine peak on the treated CoCrMo surfaces (Figure 2) reveals two types of F on the surfaces. They are $\text{p}-(\text{CF}_2=\text{CF}_2)$ and F^{-1} . At high RF power levels, the $\text{F}^{-1}/\text{p}-(\text{CF}_2=\text{CF}_2)$ ratio increased. This observation is interpreted by high dissociation energy required for C-F bond (488 KJ/mole) compared with that for C-C bond (348KJ/mole). High plasma power increased level of F^{-1} generation.

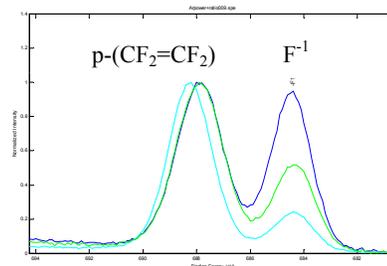


Figure 2. XPS F peaks on the CoCrMo surfaces before (red) and after 10 minutes plasma fluoridation with different power: 100w (light blue), 500w (green) and 1000w (dark blue).

During plasma fluorination, both physical sputtering and chemical reaction occur in the plasma chamber. During the sputtering, the surface PTFE polymer chains are cleaved resulting in the ejection of low-molecular weight PTFE segments. This sputtered material is then re-deposited on the CoCrMo surface, Thus, CF_2 and $\text{p}-(\text{CF}_2=\text{CF}_2)$ are observed in Figures 1 and 2.

During plasma fluorination process, low-molecular-weight PTFE segments by chain scission react with residual oxygen to form C-O and COO^- groups. High plasma power favors formation and deposition of both these oxygen-bearing carbon entities and ionic fluoride compounds while low plasma power yields high levels of fluorocarbon entities. The source for fluoride ions on the CoCrMo surface is not limited to the PTFE block. The re-deposited $\text{p}-(\text{CF}_2=\text{CF}_2)$ is also considered as a viable source.

Conclusions:

1. CoCrMo surface fluoridation can be processed with plasma treatment when Teflon material is placed in the plasma chamber.
2. Increasing the power applied for the plasma treatment can increase the ratio of $\text{F}^{-1} / \text{p}-(\text{CF}_2=\text{CF}_2)$ on the metal surface. With low power, most F containing material on the metal surface is redeposited Teflon segments, while with high power, more fluoride forms on the surface during the plasma treatment.