Titanium alloys are used as implant material for orthopaedic and dental prosthesis owing to its biocompatibility, light weight, good corrosion resistance, and mechanical properties. However, it is critically important in clinical applications, that the implant material gets bonded to the surrounding tissues. To improve the biocompatibility of titanium alloys, coatings of artificially manufactured biocompatible materials are employed. Hydroxyapatite \([\text{Ca}_10(\text{PO}_4)_6(\text{OH})_2] \text{ or HA}\) is one such 'man-made' bone material that can be used as coating on a metal implant to render bioactivities to the otherwise bioinactive implant. HA-coated titanium alloy implants have been observed to exhibit superior biocompatibility and mechanical strength. In addition to this the coating helps in preventing the corrosion of the underlying implant material and acts as a barrier for toxic metal ions that might be released from the substrate in a biological environment. HA coatings have been developed using various coating techniques such as electrophoretic deposition, thermal spraying, sputtering, pulsed laser deposition, sol-gel method, and so on. However, pure HA coating suffers from poor interfacial adhesion with the implant and easy dissolution in body fluid. This translates into HA coating disintegration under performance condition and leads to long-term instability of the coated implant.

Research carried out to improve the stability of HA coating has shown that incorporating fluorine (fluoridation) into HA reduces the solubility of the coatings while retaining the same level of biocompatibility of the pure HA coating. This is achieved by substituting OH- groups with fluorine (F) ions in the HA crystal structure. A research team headed by Sam Zhang at the School of Mechanical and Aerospace Engineering, Nanyang Technological University, Singapore has developed dense and uniform fluoridated hydroxyapatite (FHA) coatings by the sol-gel deposition on titanium alloy (Ti6Al4V) substrates. Sol-gel deposition has advantages such as composition homogeneity, low cost, ease of operation, and ease of doping of ions over other techniques used to develop HA coatings. For long-term stability the adhesion strength between the coating and substrate is a critical factor. In this study the team has studied the adhesion strength of FHA and pure HA coatings.

Initially solutions of calcium nitrate tetrahydrate \((\text{Ca(NO}_3)_2\text{H}_2\text{O})\), phosphorous pentoxide \((\text{P}_2\text{O}_5)\), and hexafluorophosphoric acid \((\text{HPF}_6)\) were used as Ca-precursor, P-precursor and F-precursor, respectively. \(\text{Ca(NO}_3)_2\text{H}_2\text{O}\) solution was first dissolved in absolute ethanol to arrive at a 2M Ca containing solution. Similarly \(\text{P}_2\text{O}_5\) was dissolved in absolute ethanol to have a 2M \(\text{P}_2\text{O}_5\) ethanol solution that was refluxed for duration of 24 h to obtain clear P-containing solution. To this solution known amount of F-precursor was added to form a "P-F" mixture. This was followed by adding Ca-containing ethanol solution to the "P-F" mixture to obtain a Ca/P ratio of 1.67. The resulting solution was refluxed for 24 hours to obtain the sol. Seven different sols of FHA \((\text{Ca}_{10}\text{(PO}_4)_6\text{F}_x(\text{OH})_{2-x})\) (with x taking values of zero, 2/6, 4/6, 6/6, 8/6, 10/6, 12/6) were prepared with different degree of fluorine substitution. Polished Ti6Al4V substrates were cleaned with acetone and deionized water before dip coating the sols. The withdrawal speed employed was 3 cm/min. The dipped coatings were dried at 150 degrees C for 15 minutes and then fired at three different temperatures of 500 degrees C, 600 degrees C, or 700 degrees C. FHA coatings of thickness 1.5 micrometers were achieved by repeating the deposition for four times.
"We found that incorporation of fluorine ion into the HA structure not only enhances the adhesion strength but also drastically reduces dissolution of the coating in simulated body fluid," Zhang tells Technical Insights.

The resultant coatings were characterized using X-ray photo electron spectroscopy and X-ray diffraction. The tests revealed that the FHA coatings were homogeneous in nature and had a Ca/P ratio ranging from 1.63 to 1.7. Scratch tests were conducted on the FHA-coated samples. Results of these tests indicated that the adhesion strength increased with increasing amount of fluorine substitution and firing temperature. It was reported that the coating adheres to the substrate 35 % better as the fluorine concentration was increased. In addition it was observed that the coating-substrate failure mode shifts from brittle to ductile nature as the content of fluorine increases.

Zhang says, "Addition of fluorine in HA has shown increased adhesion strength on Ti-alloy and reduced dissolution rate. This gives hope for long-time stability, and thus is one-step closer to clinical application."

FHA can be applied as coating on Ti6Al4V or stainless steel implant for better biocompatibility and enhanced bioactivities. That would translate to less or no rejection and faster healing.

"Currently the tests are still in lab. The work continues in collaboration with Zhejiang University, China and Singapore Institute of Manufacturing Technology," says Zhang.

Cell culture is in progress and very positive results have been obtained till date. As a next step the research group plans to conduct in vivo test on animals. So far the group has submitted two patents through Nanyang Technological University, Singapore. Details: Sam Zhang, Associate Professor, Director of Thin Film Technology Strategic Research Program, School of Mechanical and Aerospace Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798. Phone: +65-6790-4400. Fax: +65-6791-1859. E-mail: msyzhang@ntu.edu.sg.