Performance of atmospheric plasma sprayed HA coatings under dry and wet fatigue conditions

J. N. Barry, A. J. Carr, D. P. Dowling

School of Mechanical and Materials Engineering, University College Dublin, Belfield, Dublin 4;

Email: denis.dowling@ucd.ie

Keywords: Mechanical Fatigue, Biomimetic testing, Plasma Spray, Bio-medical Coatings

Abstract

Hydroxyapatite (HA) is widely used as a bio-medical coating on press-fit (cementless) orthopaedic implants to enhance the biological response of the device. Presently atmospheric plasma spray (APS) is the most widely applied technology for the deposition of such bio-medical coatings. There have been concerns however, regarding the high deposition temperatures to which the HA precursor powder is exposed during APS processing, as this can result in changes to the HA powder's crystallinity. Furthermore, concerns have been raised regarding the affect these crystalline alterations may have on the solubility of the deposited HA coating, and thus, the affect they may have on the integrity of the coating at the metal interface. The aim of this study is to evaluate the fatigue performance of APS HA coatings, carried out under both dry and wet fatigue conditions. The wet fatigue conditions were facilitated using a Simulated Body Fluid (SBF) solution, which enabled the *in vitro* simulation of the HA coating response in a typical *in vivo* environment. SEM and XRD examination of both the reference (as received) and dry samples demonstrated the coating properties were almost identical after 10 million cycles, while the evaluation of the wet samples suggested complete failure of the HA coating had occurred during testing. In conclusion, HA coating delamination during the wet fatigue testing was attributed to significant weakening of the coating, due to material loss from dissolution as a result of exposure to the SBF solution. Significantly the dissolution was found to occur both at the interface and within the coating.

Introduction

The commercial success of the atmospheric plasma spray (APS) deposition technology in the application of HA coatings is due to its high deposition rates, large coating thickness, reasonable chemical and microstructure control, mid-level deposition cost and ability to coat complex shapes. Concerns however, have been raised regarding the change in HA crystalline phase during the high temperature (≈5700 °C) APS deposition process [1]. Crystalline HA coatings have shown lower dissolution rates and enhanced long term fixation in-vivo [1, 2]. Furthermore, there are concerns regarding the effect that this enhanced dissolution may have on the integrity between the metal interface and the plasma spray coating [2].

In recent years, explanted APS HA coated devices, have shown signs of severe coating delamination [3] and third body wear [4]. The issue of delamination has been attributed to the continuous loading and unloading (or fatigue loading) of the device during normal implanted function, however, ISO standard fatigue tests performed on APS HA coatings, have shown little or no coating failure after 10

million cycles [5]. Significantly these standards require the fatigue tests be performed only in atmospheric conditions. While these conditions are suited for replication, they do not however represent the biological conditions that the implant is exposed to during normal implanted function.

This paper evaluates the long term fatigue performance of APS HA coatings carried out under both dry (atmospheric) and wet fatigue conditions. Both the dry and wet fatigue tests were performed to a modified ISO standard. In the case of the wet tests, the APS HA coating is exposed to a Simulated Body Fluid (SBF) solution during testing. The SBF solution is designed to mimic the ion concentration and pH conditions that an implanted coated device would be exposed to during normal implanted function [6]. The properties of the samples were evaluated post fatigue testing using a range of characterisation techniques. The aim of this study was to determine if the wet conditions, rather than the dry conditions, would better represent the long term response of the APS HA coatings observed during normal implanted function.

Materials & Methods

The fatigue studies were carried out using titanium alloy (grade V) cylindrical substrates machined to the dimensions detailed in Figure 1. The APS HA coatings were deposited by APS Materials Inc. (Waterford, Ireland), a commercial atmospheric plasma spray deposition company. The fatigue tests were performed using a rotating cantilever bending machine (or Wöhler tester) [7], which operates at 4700 rpm, and with an adjustable cantilever length set to 70mm.

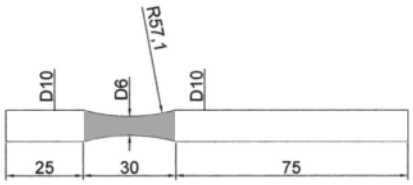

Figure 1: Fatigue substrate dimensions, with the coated section indicated in grey

Fatigue Limit

The fatigue limit is defined as the maximum value of applied alternating stress that a test sample can indefinitely endure without failure. The fatigue limit is integral to this study, as the purpose of this study is to evaluate the fatigue performance of the APS HA coatings and not that of the substrate. Knowing the fatigue limit will prevent failure of the substrate and determine the maximum fatigue stress possible to be imparted on the APS HA coatings. Through experimentation the fatigue limit of the titanium substrates was estimated to be 550 MPa, which fits well with literature [8-10].

Dry fatigue testing

The dry fatigue tests were performed under atmospheric conditions, and involved mounting the APS HA samples on the tester with the required cantilever load positioned 70mm from the centre of coated section (grey area in Figure 1). The APS HA samples were then tested to 10 million cycles, at 4700 rpm. The load was calculated as that required to develop a stress amplitude equivalent to 90 % the

fatigue limit, or 495MPa. The use of only 90 % of the fatigue limit gave further assurance that the substrates would not prematurely fail due to fatigue, and also guaranty a high level of stress could be imparted on the APS HA coating.

Wet fatigue testing

The wet fatigue tests were performed under the same fatigue parameters as the dry tests. An additional soft polymer enclosure, encapsulating the APS HA coating, facilitated the exposure of the SBF solution to the coating for the full period of testing. To insure retention of the SBF solution during the high speed testing, the soft polymer enclosure was sealed using a cyanoacrylate adhesive.

Following testing, the substrates were ultrasonically cleaned in deionised water and dried at 50 °C for 1.5 hours prior to evaluation. The surface roughness (R_a) of the HA coatings was determined using optical profilometry. Scanning Electron Microscopy (SEM) analysis was performed to examine the coating morphology and cross-section. The chemical elements present at the coated interface were determined using Energy Dispersive X-ray spectroscopy (EDX). The crystallographic structure present at the coated interface was determined using X-ray diffraction (XRD).

Results & Discussion

SEM micrographs of the tested samples established that the morphology (Figure 2) of both the reference and dry samples were almost identical. Conversely, there appeared to be little or no coating present in the micrographs of the wet samples.

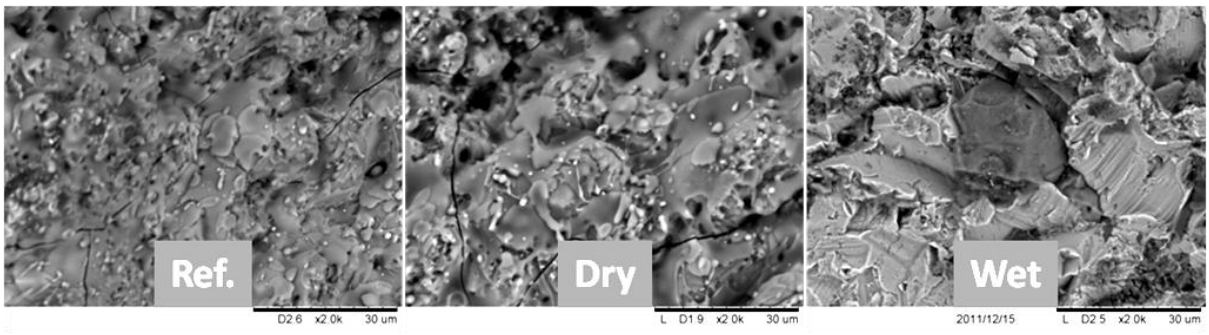

Figure 2: SEM morphological micrographs (×2000) of the Ref (as received), Dry tested and Wet tested samples.

Further investigation using XRD (Figure 3) reflected these findings, with the wet sample's spectra showing no XRD peaks related to HA and three large peaks associated with the substrate material. Furthermore, EDX analysis of the wet samples only detected trace elements of Ca and P (constituent of HA). Cross-sectional micrographs of the tested samples, verified that no HA coating was present on the wet tested samples, but significantly found that minor coating splintering had occurred in the case of the dry samples.

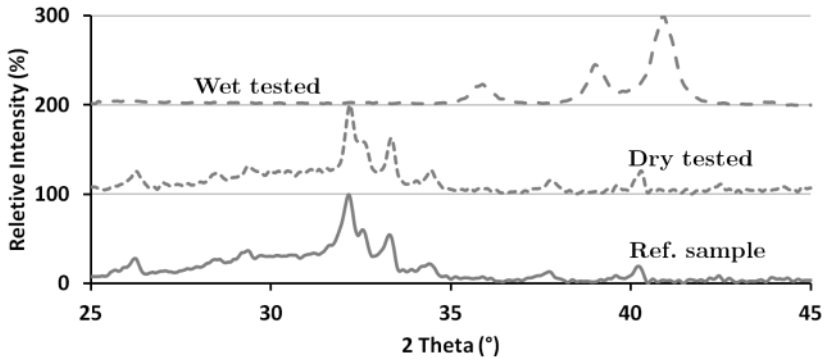

Figure 3: XRD evaluation of the Ref (as received), Dry tested and Wet tested samples.

These findings indicate that complete delamination of the APS HA coatings has occurred during wet fatigue tests, while the same fatigue parameters under dry conditions resulted in only some splinters but no coating delamination. The disparity in results for the dry and wet fatigue test conditions are due in part to the inherent HA dissolution that occurs in the presence of the SBF solution. Importantly, this dissolution would also be expected to occur within the body. An examination of the literature regarding explanted APS HA coated devices would further suggest that the tests performed with the SBF solution provide a more accurate representation of the implanted device environment. Therefore, this fatigue test methodology should provide a more accurate assessment of the long term performance of APS HA coatings in the body.

Acknowledgement

This work is supported by the Science Foundation Ireland under grant No. 08/SRC/I1411

References

1. Hench, L. and J. Wilson, *An introduction to bioceramics*1993: World Scientific Pub Co Inc.
2. Xue, W.C., et al., *In vivo evaluation of plasma sprayed hydroxyapatite coatings having different crystallinity.* Biomaterials, 2004. **25**(3): p. 415-421.
3. Heimann, R.B., *Thermal spraying of biomaterials.* Surface and Coatings Technology, 2006. **201**(5): p. 2012-2019.
4. Brown, T., et al., *2009 Nicolas Andry Award: Clinical Biomechanics of Third Body Acceleration of Total Hip Wear.* Clinical Orthopaedics and Related Research®, 2009. **467**(7): p. 1885-1897.
5. Clemens, J.A., et al., *Fatigue behavior of calcium phosphate coatings with different stability under dry and wet conditions.* J Biomed Mater Res, 1999. **48**(5): p. 741-8.
6. Kokubo, T., et al., *Solutions able to reproduce in vivo surface-structure changes in bioactive glass-ceramic A-W3.* Journal of biomedical materials research, 1990. **24**(6): p. 721-734.
7. Knez, M., et al., *A rotating bending approach for determination of low-cycle fatigue parameters.* International Journal of Fatigue, 2010. **32**(10): p. 1724-1730.
8. Callister, W., *Materials Science and Engineering: An Introduction, 7th Eds*, 2008, Wiley, 832p.(ch2) Callister WD and Reth isch DG.
9. Rack, H.J. and J.I. Qazi, *Titanium alloys for biomedical applications.* Materials Science and Engineering: C, 2006. **26**(8): p. 1269-1277.
10. Niinomi, M., *Mechanical properties of biomedical titanium alloys.* Materials Science and Engineering: A, 1998. **243**(1–2): p. 231-236.