Not All Coatings and Surface-Hardening Technologies are Created Equal

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INTRODUCTION: Metal debris and ions generated during implant wear and/or corrosion can cause metal hypersensitivity reactions in some patients[1]. Nickel, a residual element in cobalt chromium (CoCr) alloys, is one of the most frequent causes of these reactions[1]. Although the subset of patients affected by metal hypersensitivity is relatively small, there has been an increase in prevalence of knee femoral components offering nickel free solutions[2]. Titanium niobium nitride (TiNbN) and titanium nitride (TiN) coatings have been applied to CoCr and titanium implants to create a hard and chemically inert surface. However, these ceramic coatings are often poorly adhered to the implant and can delaminate or wear off over time. Ion beam-assisted physical vapor deposition (PVD) of TiN is a coating deposition process that may improve coating adhesion to the substrate. In contrast to coatings, nitrogen diffusion hardened titanium offers another solution. This surface hardening technique does not have adhesion issues, but the hardened layer is shallow (~0.2 µm). Once worn through, the underlying titanium alloy is exposed and potentially causes accelerated wear. Another nitrogen-hardening technique involves forming a TiN layer on the surface, then diffusing the nitrogen further into the substrate during a post-process step. This provides a deeper hardened zone (~35 µm), but the post-process diffusion can cause grain growth, reducing surface hardness and fatigue strength of the implant. Finally, oxidized zirconium is a solution that has been offered since 1996. Similar to nitrogen-hardened titanium, oxygen is diffused into the surface of the zirconium alloy. Once the oxygen fully saturates the surface, it transforms from a hardened metal into a ceramic. This process results in a greater depth of hardening (~5 µm) without adhesion concerns. The objective of this study was to evaluate and compare the bone cement abrasion resistance, hardening depth, and surface characteristics of these different technologies.

METHODS: Bone cement abrasion resistances of various materials were evaluated on a bespoke reciprocating bone cement abrasion tester[3]. Surfaces were tested in lactated ringer's solution for a duration of 1 million cycles. Disks were approximately 35.4 mm in diameter × 6 mm thickness. Bone cement pins were made from polymethylmethacrylate containing zirconia as a radiopaque material. Zr-2.5Nb disks (ASTM F2384) were oxidized to form a well-adhered ceramic oxide (5 µm thick) as described previously (OxZr)[4]. Titanium – 6 aluminum – 4 vanadium (Ti64) disks (ASTM F1472) were nitrogen diffusion hardened (NDH) at 593°C for 8 hrs as described in US Patent 5,192,323 with reduced nitrogen pressure instead of atmospheric pressure. The depth of nitrogen penetration and the concentration profile were measured using x-ray photoelectron spectroscopy (XPS), and results were compared to previous results [5,6]. The following disks were obtained from commercial vendors for testing: TiNbN-coated CoCrMo (via PVD, 5 µm thickness), TiN-coated Ti64 (via ion beam-assisted PVD), and Ti64 with two-step nitrogen diffusion hardening (2 step NDH) . All the samples (n=3, n = 5 for PVD TiN) were tested with a mirror-finished surface (R_a<0.05 micron). After the bone cement abrasion test, wear depth and wear volume were measured using a contact profilometer.[3] The microhardness of each surface was measured using a Knoop indenter with a load of 50 g. Five indents were made on one disk of each type and averaged. Disks were cross-sectioned, mounted, and polished to evaluate the depth of hardening via optical microscopy. One-way analysis of variance (ANOVA) with post-hoc Tukey comparison and power analysis was performed (Minitab 24.4.1) to compare results ($\alpha = 0.05$).

RESULTS: For the NDH sample, XPS analysis showed nitrogen reached a peak concentration of 7 at% at ~ 25 nm below the surface and a maximum depth of ~165 nm. Shetty reported a peak nitrogen concentration of 32 at% at 40 nm below the surface,[5] whereas a second study reported 8 at% at 7 nm below the surface[6]. Table 1 shows the surface technology, nominal or measured hardening depth, average maximum depth of the wear track (Pt), the estimated wear volume, and Knoop microhardness. Figure 1 shows a representative wear track profile for each technology after the bone cement abrasion test.

DISCUSSION: The TiN ion beam assisted coating and TiNbN PVD coating had high microhardnesses, but both wore through before the completion of the bone cement abrasion test, resulting in high wear volume. The 2-step NDH process produced highest depth of hardening; however, the surface hardness was less than other evaluated surfaces, which may have contributed to increased wear. The NDH and OxZr technologies had the lowest estimated wear volume, but the hardened surface of NDH had completely worn through, which would lead to higher wear if more cycles had been completed. In addition, the estimated wear volume of the NDH technology was still approximately 2× higher than the OxZr. Statistically significant differences are identified by groupings labeled in Table 1. Retrospective power analysis showed that the sample size was inadequate for detecting practically significant differences for hardness and wear volume. It should be noted that there was an order of magnitude difference in wear volumes between coating technologies and nitrogen diffusion hardened technologies, as well as between nitrogen diffusion hardened technologies and OxZr.

SIGNIFICANCE: Durability of the bearing surface is important for wear reduction and associated biological response from the wear debris. The ion beam assisted TiN coating performed similar to traditional TiNbN PVD coating. The 2-step NDH process provided a greater depth of hardening, but showed higher wear (and, presumably, more wear debris) compared to the NDH and OxZr technologies. Although nitrogen diffusion hardening of Ti6Al4V showed better durability compared to other technologies, the hardened layer was worn through within 1 million cycles and, thus, may not be optimal for long-term usage.

REFERENCES: 1. Lachiewicz et al., J Am Acad Orthop Surg. 24(2), 2016; 2. Xie et al., Arthroplasty Today,28, 2024; 3. Hunter et al., ASM Intl, 91-97, 2004.4. Hunter et.al., JASTM Intl, 2(7), 2005; 5. Shetty, ASTM STP 1272, 1996; 6. Venugopalan et al., Trans ORS #507, 1999.

Table 1: Summary of measurement results, mean ± standard deviation. Statistically significant differences identified in Tukey comparison are shown by grouping labels with results. In each row, metrics with different letters are significantly different.

	PVD TiN (ion beam assisted)	TiNbN	Ti64 with NDH	Ti64 with 2 step NDH	OxZr
Surface Technology	Ion beam assisted PVD coating	PVD coating	Diffusion hardened	Coating diffusion	Oxide surface transformation
Depth of Hardening (µm)	5	5	0.2	35	5
Knoop Surface Hardness	$1147 \pm 57^{B,C}$	2382 ± 114^{A}	$946 \pm 66^{C,D}$	830 ± 28^{D}	1208 ± 40^{B}
Max Wear Depth (µm)	10.50 ± 0.40^{B}	22.67 ± 2.27^{A}	2.31 ± 0.43^{C}	3.06 ± 0.58^{C}	1.23 ± 0.08^{C}
Wear Volume (mm^3)	0.26 ± 0.02^{B}	0.671 ± 0.039^{A}	0.014 ± 0.003^{C}	0.047 ± 0.006^{C}	0.006 ± 0.005^{C}

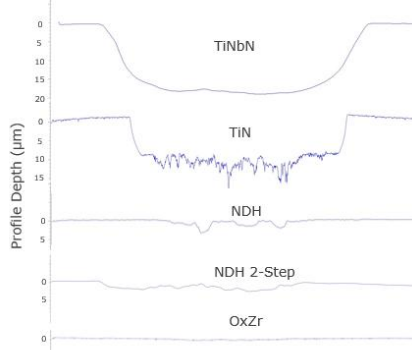

Figure 1: Representative traces across wear tracks after 1 million cycles of abrasion testing.