Metal Ions Contribute to the Material Instability of Zirconia Toughened Alumina

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INTRODUCTION: Femoral heads made from zirconia toughened alumina (ZTA) are considered to be the most advanced bioceramic currently available for total hip arthroplasty (THA). ZTA is an improvement over prior generations of medical ceramics because of its higher strength. In turn, its superior mechanical properties result from the polymorphic transformation of its zirconia phase under the tensile stress field of a propagating crack.[1,2] However, unintended transformation can also spontaneously occur by exposure of the ceramic to biologic or hydrothermal environments, resulting in the annihilation of any toughening effect.[3] Recognizing this undesirable phenomenon, ZTAs have been improved over the years, and are now less prone to transformation;[4] but positive *in vivo* confirmation of enhanced material stability is lacking. In fact, even short-term retrievals quite often reveal high amounts of transformation when compared to predictive *in vitro* models.[5] Consequently, the present investigation was undertaken to determine if metal ions present in the joint space (*e.g*., titanium, iron, *etc*.) might be responsible for triggering phase changes in the material.

METHODS: Five retrieved ZTA femoral heads were examined including four BIOLOX® *delta* (CeramTec GmbH, Plochingen, Germany) and one BIOCERAM® AZ209 (Kyocera Medical Corp., Osaka, Japan). Their respective compositions and properties are well-known.[6] Two of the BIOLOX® *delta* retrievals (Case A and B) were ceramic-on-polyethylene implants (Active Articulation™ E1® Dual Mobility Hip System, Biomet® Orthopedics, Warsaw, IN), which included an as-cast high carbon cobalt chrome molybdenum (CoCrMo) alloy press-fit metal cup (M^2a-Magnum™) with a porous plasma sprayed titanium (PPS®) outer layer. These two bearings were retrieved at 2 and 9 months after their index surgeries for infection and dislocation, respectively. The femoral head from Case A had a clean surface whereas the head from Case B was heavily stained with Ti metal. The other two BIOLOX® *delta* head retrievals (*i.e*., Cases C and D) had limited regions of similar metal staining. Case C (Ø36 mm head with a Continuum™ acetabular shell and Longevity™ PE liner, Zimmer, Warsaw, IN) was revised at 8 months, while Case D (Ø28 mm head with an X3™ PE liner and Trident™ acetabular shell, Stryker Orthopedics, Kalamazoo, MI) was revised at 23 months, both for aseptic cup loosening. Finally, Case E (Ø28 mm BIOCERAM® AZ209 ZTA head with an Aquala™ PE liner and acetabular shell, Kyocera Medical Corp., Osaka, Japan) was retrieved at 23 months for aseptic stem loosening. Case E also showed localized Ti-metal stains on its surface. Raman spectra of the main-wear (MWZ) and non-wear (NWZ) zones from these ZTA retrievals were acquired and compared with pristine components received directly from the manufacturers. Five maps were compiled for each zone consisting of 12,500 points. Monoclinic volume fractions, V_m, were then calculated from respective Raman data by means of the Katagiri equation.[7] For comparison purposes, a quantity of twelve pristine femoral heads (three of which were subjected to experimental metal staining of their surfaces) were subjected to accelerated hydrothermal ageing (*i.e*., 200 h at 121°C and 1 bar water vapor pressure) before their spectroscopic examinations.

RESULTS: Figures 1(a), (b), (c) show histograms of monoclinic phase fractions after *in vivo* exposures of 2, 9, and 23 months (Cases A, B, and E, respectively). A comparison between average values in NWZ/MWZ and the expected transformation extrapolated from *in vitro* tests is shown in Fig. 1(d) for Cases A through D. Note that significantly greater amounts of transformation were observed for MWZ in comparison to NWZ areas in all retrievals. Measured *in vivo* values were also found to be greater than predictions from *in vitro* data in every instance (*cf*. Fig. 1(d)). Since all retrievals except for Case A showed some metal surface staining, additional hydrothermal experiments were performed *in vitro* after experimental staining of pristine BIOLOX® *delta* heads with Ti. Remarkably, the metal-stained heads always showed enhanced instability and larger monoclinic fractions (comparable with *in vivo* observations). Line maps of monoclinic content in the vicinity of the *in vivo* and artificially introduced *in vitro* Ti-metal stains are shown in Fig. 2(a). The similarity of these results suggests that metal ions may have adversely affected the surface stability of ZTA. Figure 2(b) shows monoclinic volume fractions from BIOLOX® *delta* heads that were pristine, aged, or aged after Ti staining. These histograms provide a statistical foundation for the data shown in Fig. 2(a). These experiments were subsequently repeated with iron (Fe) stains with similar results.

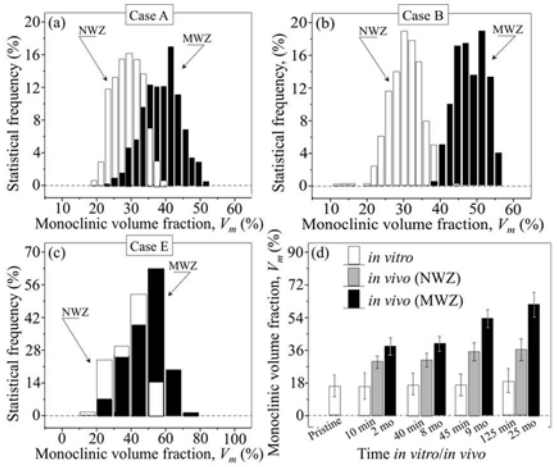

Figure 1 – Histograms of monoclinic content in retrievals: BIOLOX® *delta* in (a) and (b), and BIOCERAM® AZ209 in (c). In (d) a comparison is provided of predicted *in vitro* and average *in vivo* monoclinic contents for BIOLOX® *delta*.[1]

DISCUSSION: Our data suggest that metal staining of ZTA femoral heads leads to a discrepancy in predicted (*in vitro*) versus observed (*in vivo*) phase transformation rates. We hypothesize that enhanced phase instability may reflect a catalytic reaction at the ceramic surface (*i.e*., preferential disassociation of water, with higher hydroxyl concentrations accelerating the zirconia phase transformation). Naturally-occurring Fe-ions in the prosthetic joint space may also trigger phase instability in ZTA heads because enhanced phase transformation in one short-term stain-free retrieval (Case A) was also observed. Experiments to clarify this point are ongoing.

SIGNIFICANCE: Metal ions have an apparent detrimental role in destabilizing the zirconia phase at the surface of ZTA femoral heads which may impact mechanical or wear performance. Metal ions naturally present in the prosthetic joint space, metal staining of the head from hip instability, or metal ions released from modular taper corrosion could all contribute to ZTA instability, even in well-functioning THA prostheses. Further studies are needed to validate these observations.

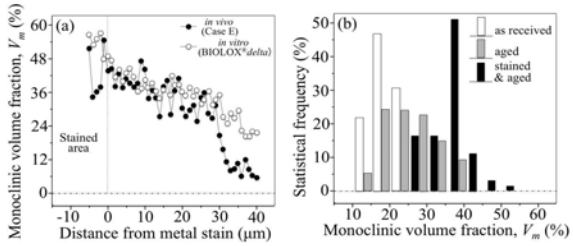

Figure 2 – (a) Line maps of monoclinic content in the vicinity of Ti-metal stains *in vivo* and artificially introduced *in vitro*; in (b), a comparison among histograms of monoclinic content recorded *in vitro* with and without Ti stains on the head surface.

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