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Corrosion-wear of β-Ti alloy TMZF (Ti-12Mo-6Zr-2Fe) in simulated body fluid

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ABSTRACT

Titanium alloys are popular metallic implant materials for use in total hip replacements. Although, α + β titanium alloys such as Ti-6Al-4V have been the most commonly used alloys, the high Young's modulus (∼110 GPa) leads to an undesirable stress shielding effect. An alternative is to use β titanium alloys that exhibit a significantly lower Young's modulus (∼70 GPa).

Femoral stems made of a β titanium alloy known as TMZF (Ti-12Mo-6Zr-2Fe (wt.%)) have been used as part of modular hip replacements since the early 2000's but these were recalled in 2011 by the US Food & Drug Administration (FDA) due to unacceptable levels of 'wear debris'. The wear was caused by small relative movement of the stem and neck at the junction where they fit together in the modular hip replacement design. In this study, the corrosion and wear properties of the TMZF alloy were investigated in simulated body fluid to identify the reason for the wear debris generation. Ti64 was used as a control for comparison. It is shown that the interaction between the surfaces of Ti64 and TMZF with simulated body fluid is very similar, both from the point of view of the products formed and the kinetics of the reaction. The dry wear behaviour of TMZF is also close to that of Ti64 and consistent with expectations based on Archard's law for abrasive wear. However, wear of Ti64 and TMZF in simulated body fluid show contrasting behaviours. A type of time-dependent wear test is used to examine the synergy between corrosion and wear of TMZF and Ti64. It is shown that the wear of TMZF accelerated rapidly in SBF whereas that of Ti64 is reduced. The critical role of the strain hardening capacity of the two materials and its role in helping the surface resist abrasion by hydroxyapatite particles formed as a result of the reaction with the SBF is discussed and recommendations are made for modifications that could be made to the TMZF alloy to improve the corrosion-wear response.

Statement of Significance

TMZF is a low modulus β-Ti alloy that has been used as the femoral stem in the Stryker modular design total hip replacement. It went into service in the early 2000's but was recalled by the FDA in 2011 due to unacceptable levels of wear debris released in the body which led to adverse physiological reactions. A large number of these implants remain in patients today.

In this contribution, we investigate the corrosion (interaction of the alloy with simulated body fluid (SBF)), dry wear and then corrosion-wear in SBF to identify the origin of the unacceptable levels of wear that led to the FDA recall of this material. We use Ti-6Al-4V as a control and demonstrate that the reaction between Ti64 and TMZF with SBF is very similar in terms of both products formed and kinetics. We also show that the dry wear behaviour of TMZF is very similar to that of Ti64 and exactly as should be expected for the hardness of this material.

However, the wear behaviours of TMZF and Ti64 are completed different in SBF and wear of TMZF is significantly accelerated in SBF. A type of time-dependent wear test is used to demonstrate the synergy between corrosion and wear and the key role of the strain hardening capacity (or lack thereof in the case of β-Ti) is discussed.

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1. Introduction

Titanium and its alloys are popular metallic implant biomaterials used in total hip replacements to treat arthritic hip joints and replace damaged bone. Commercially, α + β titanium alloys, such as Ti-6Al-4V, originally developed for aerospace applications, have become the most commonly used metallic materials because of their good biocompatibility and satisfactory mechanical strength. However, the high Young's modulus of these materials (∼110 GPa [1]) leads to a stress shielding effect, which has been identified as the main cause of aseptic loosening, a type of long-term failure of total hip replacements. During stress shielding, bone density is reduced because of the removal of normal stress from the bone by the much stiffer implant. During the last two decades much research has been devoted to the development of bulk metallic materials that have lower Young's moduli, among which β titanium alloys have attracted significant attention [2–6]. β titanium alloys are usually vanadium-free, and the principal alloying elements are niobium, molybdenum, tantalum, and iron, all of which exhibit suitable biocompatibility [7]. Lower Young's modulus is considered a great advantage of β titanium alloys (∼70 GPa [1]) in bone healing and remodelling [8,9].

In recent years, femoral stems made of β titanium alloys have been used in total hip replacements. Typical examples are the Stryker ABG II Modular and Rejuvenate Modular [10]. These two products were introduced in 2002 by Stryker, one of the major orthopaedic manufacturing companies. However, after nearly 10 years in use, they were recalled by the US Food & Drug Administration (FDA) in 2011 [11]. Unlike typical hip implant systems where the stem and neck is monoblock (Fig. 1a), the recalled implants have a modular design with separate neck and stem (Fig. 1b). The modular design provides surgeons with an additional degree of freedom in configuring an implant to fit, as best as possible, the patient. The material used for the hip stem is called Accolade® TMZF, which is a β titanium alloy (Ti-12Mo-6Zr-2Fe (wt.%)). The modular neck is made from a specially designed CoCr alloy. The reason for the recall is unacceptable levels of 'wear debris' generated by small relative movement of the stem and neck at the junction where they fit together [11]. The motion results in debris that can cause an adverse physiological response. The CoCr neck material is much harder than the TMZF stem and the wear debris

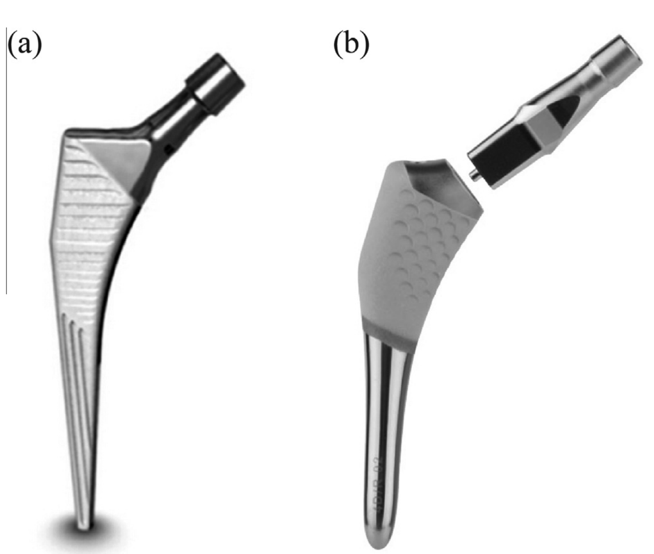

Fig. 1. (a) Hip implant with monoblock design (Adler Monoblock Stem, Oceania Orthopaedics Pty Ltd.) [13]. (b) Hip implant with modular design (ABG II Modular Femoral Stem, Stryker) [14].

is assumed to originate from the stem material under the conditions of articulating surfaces within the environment of the body. One may reasonably ask if the problem is the intrinsic modular design of the implants shown in Fig. 1 [12]. However, other modular total hip replacements using Ti-6V-4Al do not suffer from the same wear debris problem [10] and this places the focus squarely on the wear properties of the β titanium TMZF in the human body.

An understanding of the differences in the wear behaviours of the β TMZF alloy and α + β Ti64 alloy in simulated physiological environment is required to understand the long term implications of those TMZF implants that are currently implanted in patients and also for efforts to improve the wear properties of future β-Ti alloys in general. The environment inside the human body contains a great number of ions and therefore corrosion is always a primary consideration for a metal to be used in the body. Three major questions are raised:

1) Is it possible that the TMZF alloy has an unusual corrosion response in the human body and when combined with the conditions of articulating surfaces, leads to accelerated wear and the debris formation that led to the recall of the TMZF implant? Titanium gains its excellent corrosion resistance by achieving a stable, self-healing passive oxide film consisting mainly of TiO_2. It is this film that offers titanium and its alloys excellent corrosion resistance in many aqueous environments [15]. Hanawa and co-workers [16,17] report that calcium phosphate naturally forms on CP-Ti (α-Ti) and Ti64 (α + β Ti) in an electrolyte solution with pH 7.4. Similar phenomenon has also been reported on a β-Ti alloy after anodic polarization testing [18]. However, whether similar calcium phosphate can also form on TMZF (β-Ti) and if the formation kinetics are comparable to that on Ti64 is unknown.
2) Is it possible that TMZF has an intrinsic poor wear resistance compared to Ti64? The wear resistance of a metal usually correlates well with its hardness [19] – Archard's Law [20]. The Vickers hardness of TMZF is 327–345 HV [21] which is not very different to that of Ti64 (318 HV [22]). From this simplistic point of view, at least in dry conditions, TMZF may be expected to exhibit a comparable wear resistance to Ti64.
3) Is it possible that the wear and corrosion properties of TMZF in the body are conventional in their separate magnitudes but that a synergy [23–26] exists under the particular conditions of corrosion-wear in the body that leads to unacceptable wear debris for this 'system' and not for similar total hip replacement designs using Ti64? There are no reports in the scientific literature of the corrosion-wear of TMZF. Lee et al. [27] report that another β-Ti alloy, Ti-29Nb-13Ta-4.6Zr (TNTZ), exhibits higher volume loss in SBF than in dry conditions. However, the hardness of TNTZ is only 182 HV, much lower than that of Ti64 (318 HV) [22]. The poor wear resistance of TNTZ may be attributed to its low resistance to plastic deformation. TMZF is expected to exhibit improved dry wear resistance compared to TNTZ, but how it responds under the synergistic conditions of corrosion in the body are not known.

The purpose of the present study is to systematically investigate the origin of the degradation of the TMZF implant in different conditions (corrosion, dry wear, and corrosion-wear). The results are compared with those of a standard Ti64 alloy to identify the differences in the corrosion-wear behaviour between β and α + β titanium alloys. To simulate the body fluid, DMEM (Dulbecco's Modified Eagle Medium which contains the ions in body fluid)