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Research Paper

Surface toughness of silicon nitride bioceramics: II, Comparison with commercial oxide materials

Bryan J. McEntire[a], *Yuto Enomoto*[b], *Wenliang Zhu*[b], *Marco Boffelli*[b], *Elia Marin*[b], *Giuseppe Pezzotti*[b,*]

[a]AMEDICA Corporation, 1885 West 2100, South Salt Lake City, UT 84119, USA
[b]Ceramic Physics Laboratory, Kyoto Institute of Technology, Sakyo-ku, Matsugasaki, 606-8126 Kyoto, Japan

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ABSTRACT

Raman microprobe-assisted indentation, a micromechanics method validated in a companion paper, was used to compare the surface toughening behaviors of silicon nitride (Si_3N_4) and alumina-based bioceramics employed in joint arthroplasty (i.e., monolithic alumina, Al_2O_3, and yttria-stabilized zirconia (ZrO_2)-toughened alumina, ZTA). Quantitative assessments of microscopic stress fields both ahead and behind the tip of Vickers indentation cracks propagated under increasing indentation loads were systematically made using a Raman microprobe with spatial resolution on the order of a single micrometer. Concurrently, crack opening displacement (COD) profiles were monitored on the same microcracks screened by Raman spectroscopy. The Raman eye clearly visualized different mechanisms operative in toughening Si_3N_4 and ZTA bioceramics (i.e., crack-face bridging and ZrO_2 polymorphic transformation, respectively) as compared to the brittle behavior of monolithic Al_2O_3. Moreover, emphasis was placed on assessing not only the effectiveness but also the durability of such toughening effects when the biomaterials were aged in a hydrothermal environment. A significant degree of embrittlement at the biomaterial surface was recorded in the transformation-toughened ZTA, with the surface toughness reduced by exposure to the hydrothermal environment. Conversely, the Si_3N_4 biomaterial experienced a surface toughness value independent of hydrothermal attack. Crack-face bridging thus appears to be a durable surface toughening mechanism for biomaterials in joint arthroplasty.

1. Introduction

Wear of hard-on-hard bioceramic couples for artificial joints is a complex phenomenon, which is affected by surface microfracture, chemical dissolution, and local heating at the contact interface (Mattei et al., 2011; Hosseinzadeh et al., 2012). Several types of surface degradation behaviors have been observed depending on the dominant wear interactions (e.g., frictional or abrasive sliding, micro-shocks, etc.). Although the structural properties at the material's surface play a major role, wear

*Corresponding author.
E-mail address: pezzotti@kit.ac.jp (G. Pezzotti).

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performance also depends on dynamic surface responses to frictional heating, protein deposition, chemical reactions, biofilm formation, microseparation, off-stoichiometry drifts, and their possible combinations (Lu and McKellop, 1997; Kerkwijk et al., 1999; Kato and Adachi, 2002). However, wear of hard-on-hard bearings generally does not occur by a single mechanism, but is due to a combination of several factors (Adachi et al., 1997). Our present understanding of wear in ceramic-on-ceramic joints is limited, but even more limited are notions that link the phenomenologically observed wear behavior to the mechanical, tribochemical, thermal, and crystallographic properties of the material's surface. In previous papers (Pezzotti et al., 2008, 2010; Takahashi et al., 2011; Fukatsu et al., 2012), local spectroscopic probes (i.e., confocal lasers and electrons) were used to demonstrate the effects of wear on crystallographic, chemical, and off-stoichiometry alterations occurring at the very surface of oxide bioceramics employed in artificial hip joints. In particular, drifts in off-stoichiometry or phase instability and residual stresses at oxide bearing surfaces were clearly visualized after both in vivo and in vitro exposures (Pezzotti et al., 2010; Takahashi et al., 2011). Additionally, chemistry-independent damage was also observed on retrievals due to hard-on-hard micro-shock events associated with microseparation and stripe wear (Kerkwijk et al., 1999; Takahashi et al., 2011). This type of damage depends more on the surface toughness of the bioceramic than its surface chemistry and/or off-stoichiometry. Unlike bulk fracture toughness, surface toughness is prone to environmentally driven degradation. In this latter context, zirconia-toughened alumina (ZTA) biomaterials have previously been shown to undergo polymorphic transformation in a hydrothermal environment (Pezzotti et al., 2008; Chevalier et al., 2009), with local embrittlement of the material surface (Chevalier et al., 2009).

For brittle materials, wear debris are generated as a consequence of grain detachment due to repeated microseparation shocks, or by third-body abrasive particles. This phenomenon is directly related to the brittle propagation and successive coalescence of surface microcracks. Consequently, in the absence of environmental effects, wear of brittle ceramics is strongly dependent upon surface fracture toughness. An early study (Fischer et al., 1989) clearly demonstrated the effect of fracture toughness on the wear rate of zirconia under abrasive contact. Although mainly of a phenomenological nature, they showed that fracture toughness is the key parameter determining abrasive wear of brittle materials. Successive models by Evans and Wilshaw (1976) and Evans and Marshall (1980) explicitly demonstrated the roles of hardness and fracture toughness on the wear of brittle materials. They found that wear resistance was directly proportional to the products ($\text{hardness}^{1/2} \times \text{toughness}^{3/4}$) and ($\text{hardness}^{5/8} \times \text{toughness}^{1/2}$) in their analyses, respectively. Predicted wear rates from both studies agreed with experimental data. In particular, a later study Buljan and Sarin (1985) validated the theoretical dependence given by Evans and Wilshaw (1976) and indicated that Si_3N_4 was the most resistant ceramic material to abrasive wear. However, according to the phenomenological nature of the models (Evans and Wilshaw, 1976; Buljan and Sarin, 1985), the main difficulty in their practical application to biomaterials resides in the fact that they utilize bulk rather than surface toughness values. Yet, the material's surface properties might significantly differ from those in the bulk as a consequence of environmental and tribochemical effects since these can also lead to embrittlement.

In this paper, the circumstances under which hydrothermal conditions trigger a reduction of surface as compared to bulk fracture toughness are explored. Raman microprobe-assisted indentation, as validated in the companion paper, is applied to evaluate and compare the surface toughness of the most popular bioceramics nowadays employed in hip joints, before and after exposure to a hydrothermal environment. Ultimately, this procedure aims at establishing a new criterion for evaluating structural reliability at the surface of ceramic biomaterials. By conjugating micromechanics and tribochemistry, our aim is to provide new insight into the durability of hard-on-hard bearings in joint arthroplasty.

2. Experimental procedures

Three bioceramics were utilized in this study, including Si_3N_4 (MC^2®, AMEDICA Corporation, Salt Lake City, UT, USA) which is described in the companion paper, and two commercially available oxide ceramics: BIOLOX® *delta* and BIOLOX® *forte* (CeramTec, GmbH, Plochingen, Germany). BIOLOX® *delta* is a composite material (henceforth, simply referred to as ZTA) consisting of 80 vol% Al_2O_3, 17 vol% ZrO_2, and 3 vol% strontium aluminate. Y_2O_3 and Cr_2O_3 were added to the raw materials in quantities of 0.6 and 0.3 wt%, respectively, together with a minor fraction of SrO. During sintering, Y and Cr elements were mainly dissolved in the ZrO_2 and Al_2O_3 lattices, respectively. Average alumina and zirconia grain sizes in the final product were ~1.0 and ~0.3 μm, respectively. The BIOLOX® *forte* material was made of monolithic polycrystalline Al_2O_3. Impurity contents were: $(SiO_2+CaO+Na_2O) < 0.05$ wt% and $MgO < 0.25$ wt%. The average size of the alumina grains in the final component was ~1.4 μm. All tested specimens were Ø36 mm femoral heads. The three investigated biomaterials, MC^2® Si_3N_4, BIOLOX® *delta* ZTA, and BIOLOX® *forte* Al_2O_3, were autoclaved for 200 h at 121 °C under 1 bar of water-vapor pressure.

Vickers indentations were imprinted on the finely polished surfaces of the femoral heads before and after the autoclave cycle. A conventional pyramidal (Vickers) indentation tester (AVK-C1, Akashi Co., Tokyo, Japan) was used, while indentation imprints were made with loads varying between 1 and 10 kgf. The indentation load was applied for 20 s and released slowly to avoid partial detachment at the surface of the material and to minimize the occurrence of circumferential cracks around the imprint. Crack lengths and crack opening displacements (COD) profiles were then assessed by means of microscopy observation in a Schottky-emission gun scanning electron microscope (FEG-SEM, SE-4300, Hitachi Co., Tokyo, Japan).

Raman spectroscopic experiments were performed with the same equipment and under exactly the same conditions as those shown in the companion paper. The 182 cm^{-1} Raman band of Si_3N_4, related to the skeletal symmetric stretching of Si–N bonds (E_{2g} mode) (Honda et al., 1999), was selected for stress assessments because of its relatively strong intensity, which minimized the time involved with the measurements and allowed high band fitting reliability.