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Research paper

On the role of oxygen vacancies, aliovalent ions and lattice strain in the *in vivo* wear behavior of alumina hip joints

Yasuhito Takahashi[a], *Wenliang Zhu*[a], *Nobuhiko Sugano*[b], *Giuseppe Pezzotti*[a,*]

[a] *Ceramic Physics Laboratory and Research Institute for Nanoscience, Kyoto Institute of Technology, Sakyo-ku, Matsugasaki, 606-8585 Kyoto, Japan*
[b] *Department of Orthopaedic Medical Engineering, Osaka University Graduate School of Medicine, 2-2 Yamadaoka, Suita 565-0871, Japan*

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ABSTRACT

We have visualized at the nanometer scale the topological, chemical and mechanical characteristics of long-term *in vivo* exposed bearing surfaces of femoral heads made of monolithic alumina. Four self-mated alumina retrievals were studied, which were exposed in the human body for relatively long periods of time ranging between 7.7 and 10.7 yrs. Besides conventional morphological features, monitored by atomic force microscopy, the topographic distributions of point defects and lattice strain on the surface of the heads were systematically probed by collecting high spatially and spectrally resolved cathodoluminescence spectra from zones of different wear severity. Three types of optically active point-defect site could be detected: (i) oxygen vacancies; (ii) substitutional (aliovalent) cations; and, (iii) interstitial aluminum cations. These luminescent sites represent the main defects progressively developed in the alumina lattice during exposure in human hip joints. A clear evolution toward (environmentally driven) off-stoichiometry was found with progressing wear. Moreover, the shallow electro-stimulated optical probe also detailed the presence of lattice strain fields (of both elastic and plastic nature) stored in the very neighborhood of the bearing surface. The present spectroscopic characterizations enable substantiating important tribochemical interactions between bearing surfaces and *in vivo* environment as pivotal parts of progressive events of wear degradation.

1. Introduction

Monolithic alumina (Al_2O_3) is the most widespread ceramic material for bearing parts in hip joints because of its high bioinertness and biocompatibility (Christel, 1992), and a conspicuously low-friction coefficient (Khanna and Basu, 2006). However, scientists and technologists nowadays believe that its wear resistance could be further improved provided that fundamental aspects of its tribological behavior *in vivo* (partly unfolded or standing under debate) could be clarified at the nanometer scale. According to the basic principles of contact mechanics (Gao et al., 2006; Jamari et al., 2007), one could evince that the strong (ionic) lattice bond should ultimately preserve oxide ceramic surfaces from experiencing plastic flow under the moderate temperature/stress conditions of low-friction sliding developed in the human hip joint,

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[*] *Corresponding author.* Tel.: +81 75 724 7568; fax: +81 75 724 7568.
E-mail address: pezzotti@kit.ac.jp (G. Pezzotti).

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with surface asperity contacts being of a predominantly elastic nature. This is indeed the regime under which researchers have long tested alumina surfaces *in vitro* in conventional hip simulators (Tipper et al., 2002); however, the situation *in vivo* can be by far more complex. Grain-boundary microcracks and grain detachment could be observed in explanted alumina femoral head that failed due to excessive wear (Nevelos et al., 1993; Rainforth, 2004). Moreover, traces of plasticity (i.e., pyramidal slip of dislocations) could already be observed in mildly worn alumina surfaces (Barceinas-Sánchez and Rainforth, 1998; Nevelos et al., 1993; Rainforth, 2004), which were intrinsically different from those preferentially expected in bulk-crept alumina samples (i.e., prism slip) (Lagerlöf et al., 1984). In other words, fracture and deformation modes of *in vivo* exposed Al_2O_3 bearings cannot be simply explained in terms of fracture/yield stresses measured in bulk samples, which would be too high to occur in the range of stress and temperature estimated for a hip joint (Jahanmir, 2005).

Studies by Nevelos et al. (1999) revealed the important role of edge-loading wear (stripe wear) phenomena on the morphology of worn ceramic-on-ceramic hip surfaces. Mak et al. (2011), very recently, have reported about the influence of acetabular cup rim design on the contact stress during edge loading arising from micro-lateralization. Such unusually strong wear damage, including intergranular microcracking, typically develops into an elongated ellipsoidal shape as a result of a narrow line contact between femoral head and the edge of the liner. Conceivably, the repeated shocks occurring under bearing separation regime during gait involve contact stresses larger than the fracture/yield stress of the alumina lattice, thus triggering grain detachment and initiating third-body wear conditions. However, systematic microscopy and spectroscopy inspections of a number of long-term *in vivo* exposed alumina surfaces (i.e., with and without a stripe wear zone) has led the present authors to believe that the “mechanical” effect of bearing separation, although of fundamental importance, represents only one out of several factors exacerbating the degradation of alumina hip surfaces *in vivo*.

The nascent surfaces developed upon wear are proved to be extraordinarily chemically active, a variety of tribochemical reactions becoming energetically active there (Jeng and Yan, 1993; Mori, 1991). Hydrothermal environment on the surface of Al_2O_3 crystals is known to lead rather to dissociation than adsorption (Shapovalov and Truong, 2000); this latter phenomenon in turn produces hydroxyl and proton radicals, which promote the formation of surface vacancies for maintaining electrical charge neutrality (Fernandez et al., 2007; Pezzotti et al., 2010a). Under sliding conditions, the continuous formation and frictional removal of hydroxyls should repeatedly create and annihilate a population of different kinds of vacancy sites in the outer surface layers of alumina lattice, according to a mechanochemically activated process. The hydrophilicity of Al_2O_3 sliding counterparts should in principle minimize surface adsorption of proteins, and thus their consequent denaturation and irreversible unfolding (Garrett et al., 1999; Mishina and Kojima, 2008; Zeng et al., 1999). However, a scarcity of synovial fluid lubricant in ceramic-on-ceramic hip joints might create an extremely severe thermomechanical environment (Nevelos et al., 2001), in which modifications of the alumina lattice (i.e., especially in correspondence of grain boundaries) might increasingly take place. In this context, one could also hypothesize a role of protein by-products (e.g., hydrocarbons Deckman and Jahanmir, 1991) or released ions (e.g., Ca^{2+}, Mg^{2+}, and Na^{+}) on stoichiometric alterations of the alumina lattice. It is known, for example, that dilution of sodium hyaluronate (with the release of Na^{+} ions) takes place in patients affected by rheumatoid arthritis, as systematically detected by Dahl et al. (1985). Although the effect of the above tribochemical factors on the wear behavior of alumina bearings has not yet been discussed in detail, we shall show in this paper evidence of a clear interaction between body environment and alumina lattice. The ensemble of various tribochemically driven events should give, in long term, a contribution far from marginal to the lattice structure of the alumina bearing surface, thus also altering its mechanical resistance. The challenge here will be that of linking experimental evidences in order to clarify the complex cascade of chemical events (i.e., from the formation of point defects to the occurrence of plastic flow in the lattice) affecting *in vivo* wear behavior of monolithic alumina.

In a recently published study (Pezzotti et al., 2010a), we have discussed the physical origin of the improved environmental resistance of an alumina-matrix composite biomaterial using data collected by spatially and spectrally resolved cathodoluminescence (CL) spectroscopy. The CL probe was shown to be shallow on a nanometer scale (Pezzotti et al., 2010b) and, thus, capable to resolve both chemical and mechanical features on the very surface of the material, as they developed upon *in vitro* environmental exposure. Drawing upon what has been learned so far about CL emission in oxide biomaterials, we attempt here a similar analysis for *in vivo* exposed alumina hip surfaces. We concurrently monitored the concentration of point defects (i.e., oxygen vacancies, substitutional impurities, and interstitial aluminum) generated in the very neighborhood of the alumina surface and surface lattice strain with spatial resolution at the nanometer scale. We shall show that tribochemical and micromechanical information merges into the picture of a crystallographic lattice with characteristics of extreme off-stoichiometry and high compressive strain. CL spectroscopy is shown uncovering relevant and so far unexplored connections between the wear resistance of alumina and environmental factors peculiar to the human body.

2. Materials and methods

2.1. *Unused and retrieved alumina femoral heads*

Four retrieved (monolithic) alumina femoral heads were investigated, which were obtained upon revision surgeries after *in vivo* follow-up periods ranging between 7.7 and 10.7 yrs (Table 1). All analyzed femoral heads (28 mm diameter) were employed against alumina acetabular cups. Among the four investigated alumina retrievals, two were femoral heads (BIOLOX®*forte*, distributed by Cremascoli Co., Milan, Italy) that articulated against an alumina liner made of the same material and inserted into a metal backing shell; the other two femoral heads (BIOCERAM, distributed by Kyocera Co.,