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Kinetics and the role of off-stoichiometry in the environmentally driven phase transformation of commercially available zirconia femoral heads

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ABSTRACT

The low-temperature polymorphic transformation behavior of two types of commercially available femoral head, both made of 3 mol.% Y_2O_3-stabilized tetragonal ZrO_2 polycrystals (3Y-TZP), was examined by in vitro experiments. Both materials contained a small amount (0.25 wt.%) of Al_2O_3, but they differed slightly in their SiO_2 impurity content, in the morphology and crystallinity of the dispersed Al_2O_3 phase, and in grain size. In vitro experiments were conducted in a water-vapor environment at temperatures in the range 90–134 °C and for periods of time up to 500 h. Despite the materials having the same nominal composition, quite different behaviors were found in the hydrothermal environment for the two types of femoral head investigated. A phenomenological description of the kinetics of monoclinic nuclei formation/growth led to the experimental determination of activation energy values for the environmentally driven polymorphic transformation. From the material physics viewpoint, cathodoluminescence spectroscopy enabled us to rationalize the role of surface stoichiometry on the mechanisms leading to polymorphic transformation. Spectroscopic experiments unveiled some new relevant aspects of surface off-stoichiometry, which lie behind the different phase transformation kinetics experienced by the investigated femoral heads.

1. Introduction

Zirconia femoral heads have been used successfully, but there are real concerns regarding the polymorphic transformation on their surface: surgeons are uneasy that such transformation would increase the roughness of the femoral head with detrimental effects on the wear response of the polyethylene acetabular cup. Materials provided by different makers have proved to vary widely in quality [1,2], sometimes with catastrophic consequences [2]. It is thus mandatory to understand which material performs better and why these differences arise. In this context, the phenomenology of the phase stability of biomedical ZrO_2 exposed to a hydrothermal environment has been successfully rationalized and modeled according to the formation and successive growth/coalescence of monoclinic nuclei on the material surface [3,4]. Experimental assessments of ZrO_2 phase stability entail exposures of the sample for increasing periods of time in an autoclave at systematically increasing temperatures. The effects of such treatments are then rationalized according to a two-parameter equation quantitatively describing both the nucleation and growth rates of the monoclinic domains formed on the sample surface [4,5]. The equation stems from a crystallographic model, referred to as the Mehl–Avrami–Johnson (MAJ) model [6], which enables rationalization of the phenomenological evolution of the surface over the course of polymorphic transformation. The application of the MAJ model ultimately leads to the establishment of a value of thermal activation energy for hydrothermal degradation in polycrystalline ZrO_2, through which extrapolations can be made of the expected monoclinic fractions as a function of exposure time in vivo [5,7]. Such estimates of in vivo lifetime are popular because they provide an easily understandable ground of comparison among different ZrO_2 materials, although they unfortunately are not necessarily accurate due to a lack of dynamic effects (e.g. surface friction and local impingements actually occurring in the joints). In particular, the temperature reached with in vivo contact between zirconia head and polyethylene acetabular cup can be quite high (due to the relatively poor thermal conductivity of zirconia compared to alumina), and this makes it difficult a reliable extrapolation from in vitro to in vivo data, when it is only based on the MAJ paradigm [8]. Furthermore, the MAJ model builds solely upon phenomenological knowledge, while a truly improved path of understanding would provide a

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physical insight into the elementary processes behind the observed degradation law.

In the last few years, significant progress has been made in cathodoluminescence (CL) characterizations of ceramic materials through the development of spectrally and spatially resolved analyses [9–13]. The application of CL to bioceramics is prospering at present [11–13], but further advances are required to improve concepts concerning the quantification of stoichiometric effects on joint surfaces and their quantitative link to the kinetic processes occurring both in vitro and in vivo. In recent studies [12,13], we suggested that the key to further progress definitely resides in the full clarification of the role of oxygen off-stoichiometry on both frictional effects and wear resistance of bioceramic surfaces. In this context, CL spectroscopy can be extremely efficient in visualizing surface stoichiometry in oxide ceramics [14], and it is gradually establishing itself as a unique analytical tool for differentiating chemical and mechanical phenomena on biomaterial surfaces down to the nanometer scale. Previous results of a physical chemistry study into the formation of various states of surface oxygen produced upon aging alumina–zirconia composites in a water-vapor atmosphere [12] provided clear experimental evidence that a number of slightly different (defective) oxygen sites play a prominent role in delaying polymorphic transformation, although their common denominator is to act as surface charge compensators.

With the above background in mind, we attempt here to link CL characterizations to the more conventional outputs of a MAJ analysis of environmentally driven tetragonal-to-monoclinic ($t \rightarrow m$) ZrO_2 transformation. Two types of commercially available 3 mol.% Y_2O_3-stabilized tetragonal ZrO_2 polycrystals (3Y-TZP) femoral head, manufactured by different makers, were characterized and compared with respect to their $t \rightarrow m$ transformation rates and surface oxygen stoichiometry variations upon increasingly longer in vitro exposures to a hydrothermal environment. CL data are shown to bring about peculiar features of the ionic disorder of the femoral head surfaces and to provide hitherto missing details in the complex ensemble of environmentally driven events occurring in the lattice of metastable zirconia surfaces. Through spectrally resolved CL assessments, we first confirm the notion that annihilation of oxygen vacancies in the 3Y-TZP lattice is the main chemical driving force for phase transformation. In addition, taking advantage of the high spatial resolution of the CL probe, we disclose new topological information about different chemical and physical states of the 3Y-TZP and alumina phases, this latter being a stabilizing agent in the 3Y-TZP microstructural networks. The physicochemical state of both zirconia and alumina lattice is directly linked to the manufacturing procedure and covers a key role in the hydrothermal behavior of 3Y-TZP biomedical components.

2. Experimental procedures

Four unused 3Y-TZP femoral heads for each of two types of commercially available artificial hip implants were examined in this study. The samples were 26-mm-sized femoral heads manufactured by Japan Medical Materials in 2007 (type A) and 22-mm-sized femoral heads manufactured by NGK in 2007 (type B). Despite nominally having the same composition (both include a fraction of 0.25 wt.% of Al_2O_3 dopant), the two investigated 3Y-TZP samples differed distinctly in their average grain size (≈330 and 690 nm for samples A and B, respectively), impurity concentration (in particular SiO_2) and processing temperature. Fig. 1(a) and (b) shows the microstructures of samples A and B, respectively. Histograms of grain size, average values and standard deviations for both materials are also given in the inset to the respective micrographs. Samples were cut into several pieces and each piece was subjected separately to hydrothermal cycles of different duration and temperature. Hydrothermal acceleration tests were conducted by placing the samples in an autoclave at temperatures between 90 °C (363 K) and 134 °C (407 K) under water-vapor pressure ranging from ambient pressure to 0.31 MPa for periods of time ranging between 0 and 500 h, in order to simulate in vitro the effect of environmental aging in the human body. Data for a 3Y-TZP belonging to an old generation of hip prosthesis (26-mm-sized ball manufactured by Norton Desmarquest in 1995; sample C) is also shown for comparison.

Monoclinic phase fractions were systematically collected by Raman spectroscopy and evaluated from relative band intensities according to the equation proposed by Katagiri et al. [15]. Raman spectra were collected from relatively large areas ($100 \times 100\ \mu m^2$) randomly selected on the samples. All spectra were taken at room temperature using a triple monochromator (T-64000, Jobin-Ivon/Horiba Group, Kyoto, Japan) equipped with a charge-coupled device (CCD) detector, and analyzed by using commercially available software (Labspec, Horiba/Jobin-Yvon, Kyoto, Japan). A confocal configuration of the Raman probe was adopted throughout the experiments, which involved the use of a 100× objective lens. The numerical objective aperture, the confocal pinhole diameter and the focal length of the objective lens were: NA = 0.9, $\Phi = 100\ \mu m$ and $f = 0.3$ mm, respectively. The penetration depth of the confocal probe could be confined to few microns and was comparable with that obtained by conventional X-ray analyses [16].

CL spectra were collected in a field-emission gun scanning electron microscope (SE-4300, Hitachi Co., Tokyo, Japan) equipped with a CL device. Electron irradiation of all samples was made with acceleration voltages of 5 kV. Data were averaged on several maps, typically $30 \times 30\ \mu m^2$, randomly located on each sample. Preliminary calibrations (based on monitoring the stability of the CL spectra with respect to electron irradiation time) proved that the selected acceleration voltage was below the threshold for perturbation of the stoichiometric structure of both materials by the electron beam. The CL device consisted of an ellipsoidal mirror and a bundle of optical fibers, which enabled to collect and to transmit the CL emission into a highly spectrally resolved monochromator (Triax 320, Jobin-Yvon/Horiba Group, Tokyo, Japan). A grating of 150 g mm^{-1} was used throughout the experiments. A liquid-nitrogen-cooled 1024×256 pixels CCD camera was used to analyze the CL emission of the material. Spectral lines were analyzed with the same software package as mentioned above for Raman spectroscopy. According to quantitative calibrations of the CL probe response function by means of previously reported methods [10,14,17], the CL probe was found to be Gaussian in nature, with a size (for 90% emission) in the order of 500 nm in both depth and plane.

3. Results and discussion

3.1. Phenomenological MAJ analyses of hydrothermal test results

Fig. 2(a) and (b) shows the monoclinic volume fraction, V_m, as detected on the surface of femoral heads A and B, respectively, under different hydrothermal conditions. Plots of V_m vs. aging time, t, are given in a semi-logarithmic scale for different aging temperatures. Data are then rationalized with a best-fitting procedure using the MAJ equation [3,4] as a trial function:

$$V_m = a[1 - \exp(bt)^n] \qquad (1)$$

where t is the duration of the hydrothermal cycle, a is a constant that equals 1 when the initial monolithic fraction is zero, b is a parameter that is directly proportional to the $1/n$ power of the nucleation rate of monoclinic nuclei per unit time and area, and n is an exponent which ranges between 0.3 and 4 [5,6]. The parameter