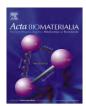
Acta Biomaterialia 8 (2012) 1639-1647

Contents lists available at SciVerse ScienceDirect

Acta Biomaterialia



journal homepage: www.elsevier.com/locate/actabiomat

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

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ARTICLE INFO

Article history: Received 13 September 2011 Received in revised form 6 December 2011 Accepted 12 December 2011 Available online 16 December 2011

Keywords: Zirconia femoral heads Cathodoluminescence spectroscopy Phase transformation Off-stoichiometry Hydrothermal acceleration test

ABSTRACT

The low-temperature polymorphic transformation behavior of two types of commercially available femoral head, both made of 3 mol.% Y₂O₃-stabilized tetragonal ZrO₂ polycrystals (3Y-TZP), was examined by in vitro experiments. Both materials contained a small amount (0.25 wt.%) of Al₂O₃, but they differed slightly in their SiO₂ impurity content, in the morphology and crystallinity of the dispersed Al₂O₃ 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.

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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 ZrO₂ 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 ZrO₂ 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

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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 MAI model ultimately leads to the establishment of a value of thermal activation energy for hydrothermal degradation in polycrystalline ZrO₂, 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 ZrO₂ 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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