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Assessment of low-temperature degradation of Y-TZP ceramics based on Raman-spectroscopic analysis and hardness indentation

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Abstract

This paper focuses on the analysis of hydrothermally induced phase transformation of yttria-stabilized tetragonal polycrystalline zirconia (Y-TZP) and its influence on the hardness. Due to the hydrothermal exposure and the accompanied low-temperature degradation (LTD), a micro-cracked transformation zone is generated at the surface and progresses into the subjacent material. Raman-spectroscopic analysis of hydrothermally loaded and cross-sectioned samples revealed complete phase transformation within this zone. Its depth as well as its temperature-dependent growth rate was verified. Raman-spectroscopic measurements at the surfaces were correlated with the progression of the transformation zone. An efficient model, which assumes one extinction coefficient for tetragonal and monoclinic microstructure, enables to determine the depth of the transformation zone from the measured Raman signals. Furthermore, an exponentially decreasing Vickers hardness with increasing depth was determined. Finally, a differently sintered Y-TZP ceramic revealed enhanced resistance against LTD for the same hydrothermal loading conditions.

Keywords: Y-TZP; Low-temperature degradation; Vickers hardness; Phase transformation; Raman-spectroscopy

1. Introduction

Yttria-stabilized tetragonal zirconia polycrystalline (Y-TZP) ceramics are promising materials for many technical applications as they provide a very high hardness and fracture toughness and mechanical strength.[1–4] Furthermore, due to their corrosion and wear resistance and biocompatibility, they are utilized for artificial femoral heads and dental restorations.[1,5] The reliability of some zirconia ceramics is still limited by undesired phase transformation in contact with aqueous solutions which is known as "low-temperature degradation" (LTD). This degradation is characterized by nucleation and growth of a transformed and destabilized zone from the hydrothermally loaded surface into the bulk material.[6] Due to the accompanied intergranular micro-cracking, LTD causes a loss of mechanical strength.[7] Extensive research on LTD of zirconia ceramics has been done in recent years.[6,8] In this context, research mainly focused on microstructural features, which affect the resistance to degradation. The addition of alumina to zirconia is for instance a suitable method to decelerate the aging process.[9] Further promising approaches are the decrease of both, the grain size and tensile residual stresses within the material.[6] An excellent review was published by Basu,[2] which generally summarizes different microstructural features that have an impact on the phase transformation. In addition, Chevalier[6] investigated the characteristic features of LTD. In summary, it can be stated that the production of aging-resistant zirconia ceramics requires an accurate setting of relevant process stages like powder mixing, sintering and machining.

In general, the experimental examination of LTD is carried out using hydrothermal ageing experiments. Subsequent investigations enable the quantification of the ratio of tetragonal and transformed monoclinic phases. Here, μ-Raman-spectroscopy has become a widely used method as it is very sensitive to monoclinic zirconia and offers a high spatial resolution.[10,11]

Based on previous research, mathematical correlations were identified between the transformed monoclinic phase content V_m and both the absolute hydrothermal loading temperature T and

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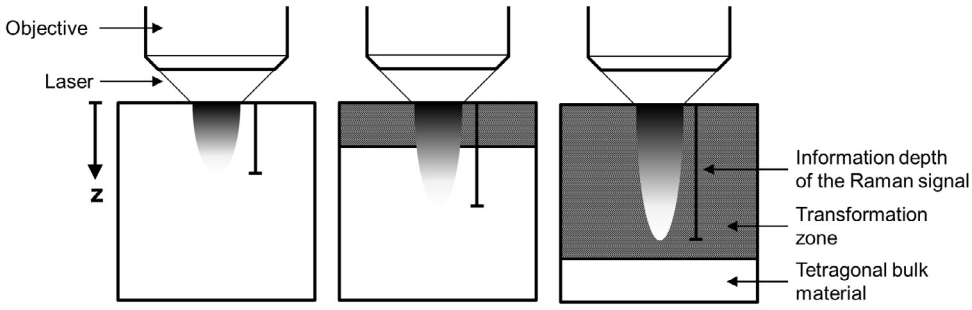

Fig. 1. Raman signals are detected in the bulk material as well as in the transformed zone for hydrothermally loaded samples. It is expected that the information depths change due to the different absorption coefficients and thicknesses of the zones.

time of exposure to moisture t. On the basis of surface analysis it was concluded that the transformation kinetics follow the Mehl–Avrami–Johnson (MAJ) law as depicted in Eq. (1):[10,12]

$$V_m = 1 - e^{-(b\cdot t)^n} \quad (1)$$

where the Avrami-exponent n depends on the nucleation-and-growth kinetics of the aging process with typical values between 0.3 and 3.5.[13] The reaction rate constant b corresponds to the Arrhenius law in Eq. (2):

$$b = b_0 \cdot e^{-Q/R\cdot T} \quad (2)$$

where R is the gas constant and b_0 is a constant pre-exponential factor that refers to the reaction mechanism of the transformation process. Q is the activation energy of the tetragonal to monoclinic transformation, which depends on both temperature and microstructure.[14]

Nevertheless, conclusions about the actually existing phase contents from Raman-spectroscopic measurements have to be drawn carefully. In fact, the detected Raman signals originate not only from the surface of zirconia samples but from subsurface areas as well. In that regard, Presser et al.[15] state that the information depth in a Raman analysis depends on material and instrumental parameters as well as the microscope setup and may therefore extend "to several tens of μm"[15] for a non-degraded Y-TZP ceramic.

In order to determine phase transformation beneath the surface, Muñoz-Tabares et al.[7] experimentally investigated cross-sections of hydrothermally loaded zirconia ceramics. While a high value of the monoclinic content was detected close to the surface, a steep gradient was observed at a certain depth where the monoclinic phase content dropped to almost zero. The gradual change from the saturated value of monoclinic phase to untransformed tetragonal structure occurs within a short distance of about 15 μm. This observation leads to the assumption that hydrothermally loaded ceramics may consist of a highly transformed zone with high monoclinic phase content and sharp transition to the untransformed bulk. Further investigations by Keuper et al.[16] using SEM/EBSD techniques yielded evidence that the transformation front is rather sharp.

As Raman signals are obtained from certain depths in the material and the surface-near areas of hydrothermally loaded samples are expected to be completely transformed, Raman-spectroscopic measurements on the surfaces can be illustrated as depicted in Fig. 1.

For a small transformation depth it is clear that a considerable part of the measured Raman intensity is detected from non-transformed subsurface areas. As the transformation front progresses into the bulk material as a consequence of further degradation, the ratio of transformed monoclinic zirconia within the Raman-probe volume increases. Taking this circumstance into account, it becomes clear that for an accurate characterization of the growth behavior of the transformation zone careful interpretation of the Raman-data is necessary. Only with this knowledge of depth-dependent signal response, Raman-spectroscopic measurements on the surfaces can be interpreted correctly and used to reliably determine the depth of the transformation zone without further sample preparations.

The objective of this work was to quantify and compare the phase transformation rates of two differently processed Y-TZP ceramics after defined hydrothermal loading conditions. Therefore, the size of transformation zones and their microstructures were characterized via optical microscopy and SEM after cross-sectioning of the degraded samples. Raman-spectroscopy was applied on the surfaces after hydrothermal loading as well as within the bulk material of cross-sectioned samples. Moreover, the materials' macro-hardness was investigated via Vickers indentation in order to examine the impact of hydrothermal loading on the mechanical response. The results of these three investigations were correlated to describe the impact of LTD on the material.

2. Materials and methods

Two differently sintered high strength zirconia ceramics (3 mol.% yttria, 0.2–0.3 wt.% alumina, FCT Hartbearbeitungs GmbH, Sonneberg, Germany) were investigated: On the one hand Y-TZP standard material exhibiting a grain size of 0.4 μm and on the other hand HY-TZP with an average grain size of 0.28 μm. The "H" refers to a modified sintering process, including an additional hot isostatic pressing step.

The experiments were conducted on rectangular bending bar samples with dimensions of 3 mm × 4 mm × 20 mm. The 4 mm × 20 mm faces of the bending bars were polished to ensure accurate Vickers indentations according to industrial standards.[17] Polishing was carried out as a multistage process with gradually different fine-grained diamond suspensions for