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Ageing Behavior of Injection-Molded ZTA Ceramics as a Function of Stabilizer Content

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Abstract

ZTA (zirconia-toughened alumina) ceramics are interesting materials for biomedical implants. High-quality implants are currently produced by means of cold isostatic pressing. The production of ZTA ceramic components by injection molding enables their mass production and an improvement in the cost and quality of complex near-net-shaped ceramic components. Injection-molded and hot-pressed ZTA materials with 10 vol% zirconia stabilized with 0, 1.5 and 3 mol% yttria were prepared and aged in an autoclave in water vapor at 134 °C for up to 48 h, corresponding to ~ 175 years *in vivo*. The phase compositions of the aged samples were examined by means of X-ray diffraction. In both experiments, it was shown that the ageing resistance of ZTA materials rises significantly with increasing stabilizer content. Compared to injection-molded and pressureless-sintered materials, fully dense hot-pressed ZTAs have shown improved long-term ageing stability. The ageing behavior of ZTA is obviously dependent on the forming process, relative density and yttria content.

Keywords: ZTA, ceramic injection molding, ageing behavior, mechanical properties

I. Introduction

In orthopedic applications, ceramic materials offer an advantage over metal-based components thanks to their reduced wear rates and excellent biocompatibility. On the other hand, the brittleness of ceramics and possible catastrophic failure *in vivo* is still a major concern in the field of ceramic processing. The excellent mechanical and wear properties of zirconia-toughened alumina (ZTA) make it a very interesting material for biomedical applications. ZTA can replace alumina in many different applications owing to the enhancement of flexural strength, fracture toughness and fatigue resistance [1].

The fracture toughness of ZTA is enhanced mainly by two mechanisms, transformation toughening and microcracking. The stress-induced transformation of dispersed tetragonal zirconia grains to monoclinic grains causes compressive stresses at the crack tip owing to the volumetric expansion of zirconia. Therefore fracture toughness increases as a result of crack tip shielding; the slow crack growth resistance of the composite is also improved [2]. Microcrack toughening is induced by the addition of large monoclinic zirconia grains that transform from tetragonal to monoclinic during cooling from sintering temperature leaving microcracks in the microstructure. In ZTA with a very low fraction of zirconia (~2 vol%) another toughening mechanism based on residual compressive stress in alumina grains containing intragranular zirconia inclusion was observed [3].

Many recent studies are concerned with ageing or low-temperature degradation (LTD) of zirconia and zirconia composites used in hip implants. This concern was raised especially after the failure events of Prozyr® femoral heads [4]. Tetragonal stabilized zirconia ceramics (Y-TZP) were considered attractive ceramic materials for hip implants because of their higher strength and fracture toughness compared to alumina. ZTA nanocomposites containing 10 vol% ZrO_2 nanoparticles (monoclinic and tetragonal) showed no deterioration of the zirconia phase after 40 h of ageing at 134 °C in saturated water vapor [5], Y-TZP exposed for the same time period shows severe hydrothermal instability, and complete conversion to monoclinic at the surface. The ageing resistance of Y-TZP depends on the amount and homogeneous distribution of yttria in the Y-TZP [6]. The severe ageing of 3Y-TZP in an autoclave decreases the flexural strength slightly and increases the Weibull modulus sharply owing to surface degradation [7]. Moreover, the wear behavior of 3Y-TZP is also influenced by increasing the grain pullouts and producing microcracks beneath the wear zone [8]. Alumina addition to Y-TZP is not only beneficial in terms of higher strength, it also enhances the ageing resistance drastically. Schneider *et al.* studied the ageing behavior of alumina-toughened zirconia (ATZ) composed of 80 wt% 3Y-TZP and achieved a lower transformation rate compared to Y-TZP ceram-

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ics [9]. Degradation under hydrothermal conditions can be reduced with the use of yttria-coated zirconia powders and forming an yttria gradient during sintering [10].

On the alumina-rich side of the zirconia-alumina system, the ageing of the zirconia can be at least theoretically eliminated by perfect dispersion of zirconia in the alumina matrix. The ideal ZTA for biomedical applications should contain perfectly homogeneously dispersed and isolated zirconia grains with a size below its transformation threshold. The absolute value of this transformation threshold – usually around 0.5 μm – is strongly dependent on stabilization, the local stress state and location of the zirconia grains. Doping zirconia grains with yttria is not essential in ZTA if the zirconia content is well dispersed and the zirconia fraction is kept below the percolation threshold of ~16 vol%, practically ~10 vol% can be added. It was claimed that the absence of yttria avoids the creation of oxygen vacancies in the zirconia lattice and reduces the diffusion of water radicals [11].

Water diffusion develops tensile stresses in surface grains, and destabilizes the tetragonal phase. Transformation begins mainly at grain corners where maximum stresses take place and progresses through the grain. In that case martensitic transformation spreads to the surrounding grains and the stresses generated owing to transformation can induce microcracking, making it easier for water to diffuse inside the bulk of the material [5]. As a result of transformation, surface uplift takes place owing to volume increase and this leads to surface roughening and microcracking of zirconia components [12]. In case of isolated zirconia grains, the transformation is restricted to the individual grains and does not protrude into the bulk. An important point to be considered in composite ceramics consisting of two materials with different CTE is the effect of cooling stress. In case of ZTA it was shown by applying an analytical solution that in ZTA without phase transformation, alumina is under compressive hydrostatic stress and zirconia is under tensile stress. With phase transformation this cooling stress can be lowered. After passing a stress neutral state at ~20 % of transformed zirconia the stress situation changes to the opposite. Zirconia under tension is more transformable, thus in ZTA a certain amount of monoclinic can be present in the absence of operating stress right after sintering [13, 14].

The competitive increasing demand on ceramic components forces manufacturers to reduce costs. Mass production of complex components is a very challenging issue. Ceramic injection molding (CIM) is a processing technology that allows the mass production of near-net-shape ceramic parts with high precision [15, 16]. Injection-molded ZTA ceramics with high ageing resistance are not only required for biomedical implants like dental screws. Interesting applications could also be complex components in mechanical engineering operating under high load and in abrasive conditions and moist atmospheres. The process cycle of CIM is much more complex compared to e.g. pressing processes. The binder content in the ceramic feedstock for injection molding has to be optimized to enhance the rheological properties of the feedstock and achieve near-net-shape parts. Binder burn-out must be performed with care so as not to introduce microstructural defects caused by even bloating. Quality control plays an important role to ensure that the mold filling cycle is perfectly accomplished, achieving high dimensional accuracy and a green density within the desired range. In this study the potential of the injection molding process with subsequent debinding and pressureless sintering to produce ZTA ceramics with sufficient quality for implants was investigated with a focus on studying the ageing behavior of injection-molded ZTA components with different stabilizer content. Hot-pressed samples were used as a benchmark.

II. Experimental

ZTA feedstocks with 10 vol% ZrO_2 and different stabilizer content (0, 1.5 and 3 mol% yttria) were prepared for processing by means of injection molding and hot pressing. ZTA was prepared from high-purity submicron size SPA0.5 α-alumina powder, d_{50} = 0.4 μm, SSA = 8 m²/g (Sasol North America, USA), 3 mol% yttria-stabilized zirconia, d_{50} = 350 nm, SSA = 7 m²/g (TZ-3YSE, Tosoh, Japan) and pure zirconia, d_{50} = 250 nm, SSA = 16 m²/g (TZ-0, Tosoh, Japan). The ZTA powder recipes are listed in Table 1. The ZTA feedstocks for injection molding were prepared by mixing the powder recipes with binder in a sigma blade mixer (Hermann Linden Maschinenfabrik, Marienheide, Germany) at 140 °C. The binder used was Licomont EK 583 G (EmBe products & service GmbH, Thierhaupten, Germany), a polyethylene-wax-based binder system that is partially soluble in water. The binder content and processing were optimized based on pre-existing results [16]. Binder was added to achieve a binder content of 43 vol% which was chosen to avoid binder segregation or insufficient flowability caused by too high or too low binder content. To further enhance the homogeneity, the ZTA feedstocks were extruded in a twin screw at 140 °C and 150 rpm (Thermofisher Scientific, Germany). A hydraulic injection-molding machine (Dr Boy 50M, Germany) was used to manufacture plates (40 x 30 x 3 mm³) at an injection pressure of 800 – 1000 bar, 65 °C mold temperature and a plastification temperature of 150 °C. The debinding and presintering process has been described in detail elsewhere [16]. The injection-molded ZTA (IM-ZTA) plates were pressureless-sintered in air at 1500 °C for 2 h in an electrically heated chamber furnace (Thermconcept, Germany). The hot-pressed ZTA feedstocks were prepared by milling the ZTA recipes (Table 1) in 200 g 2-propanol using an attrition mill at 500 rpm. The ZTA feedstocks were milled using 5 and 1 mm Y-TZP balls for 4 and 2 h respectively. The powders were dried at 85 °C and screened ready for pressing. The ZTA feedstocks were hot-pressed (KCE, Germany) in a graphite die to form circular disks of 40 mm in diameter. The disks were processed at 1500 °C under 60 MPa for 2 h soaking.

In this study, the ageing experiments were conducted in an autoclave for 6, 12, 24 and 48 h at 134 °C, at 2 bar pressure. This hydrothermal treatment induces phase transformation at the surface of the specimen and allows the quantitative measurement of the monoclinic phase fraction by means of X-ray diffraction (XRD). Ageing for 1 h in an autoclave at 134 °C is considered to be equivalent to three to four years *in vivo* [17]. Stabilized and unstabilized

ZTA materials processed by means of injection molding and hot pressing were ground and polished to a 1-μm finish in preparation for ageing experiments and mechanical characterization. The injection-molded ZTA samples were cut into 5 bars measuring 4 mm in width using a diamond wheel (Struers Accutom 50, Germany), the sides and edges of the bending bars were beveled using a 40-μm diamond disk and polished manually to remove defects induced during cutting. 3-point bending tests were conducted according to DIN EN 6872 standards. Fracture toughness was calculated from the size of HV_{10} (Bareiss, Germany) indents and length of Palmquist cracks according to Niihara's formula [18]. Crack length was measured immediately after indentation to avoid the influence of subcritical crack growth.

Table 1: The recipes of the ZTA feedstocks.

Feedstock	Al_2O_3 [m%]	TZ-0 [m%]	TZ-3YSE [m%]
ZTA-0Y	85	15	0
ZTA-1.5Y	85	7.5	7.5
ZTA-3Y	85	0	15

The method is known to lead to excessively high values, in the present case the toughness was only used for the purpose of comparison. Microhardness $HV_{0.1}$ and Young's modulus were measured using a microindenter (Fischerscope, Germany). The phase composition was determined from X-ray diffraction data obtained with a diffractometer using Cu-Kα radiation (Bruker AXS D8 Advance, Germany). The monoclinic phase fraction after ageing was determined by integrating the areas under the diffractometer peaks for tetragonal (101) and monoclinic peaks (111 and -111) as described by Toraya *et al.* [19]. Diffractometer scans were obtained from 26° to 33° at a scan speed of 0.6°/min and a step size of 0.01°. The density measurements of the polished ZTA were calculated before ageing using the Archimedes method in ethanol. The aged samples were thermally etched in air at 1400 °C/1 h and the microstructure was investigated with SEM.

III. Results and Discussion

The microstructures of the obtained ZTA are principally dependent on the processing method. A homogeneous dispersion of zirconia grains in the alumina matrix is observed in the injection-molded ZTA (Fig. 1 a). The zirconia grain size is ~0.4 μm and is much finer than the alumina grain size (~1 μm). The zirconia grains in the injection-molded ZTA are seen mainly in intergranular positions within the alumina matrix. Some perfectly modular zirconia grains were also found within the alumina grains. While Fig. 1 a shows a locally perfect microstructure, the porosity distribution and incomplete densification (~94–95 %) can be seen much better in images with smaller magnification. In Fig. 4, which shows an aged surface, it becomes evident that local accumulations of porosity exist with dense regions in between. On the other hand, the complete densification (99 % relative density) of the hot-pressed ZTA at 1500 °C is clearly seen in Fig. 1 b, while the zirconia distribution is fairly homogeneous, the hot-pressed samples also contain large zirconia aggregates which are not present in the injection molded material (Fig. 5). The applied compounding technology for the hot pressing feedstocks – milling in alcohol without additives was not capable of perfectly dispersing the zirconia grains. In the homogeneous regions the zirconia grain sizes of hot-pressed ZTA were in the same range as in the injection-molded material, which is not too surprising as both were fired at the same temperature and dwell.

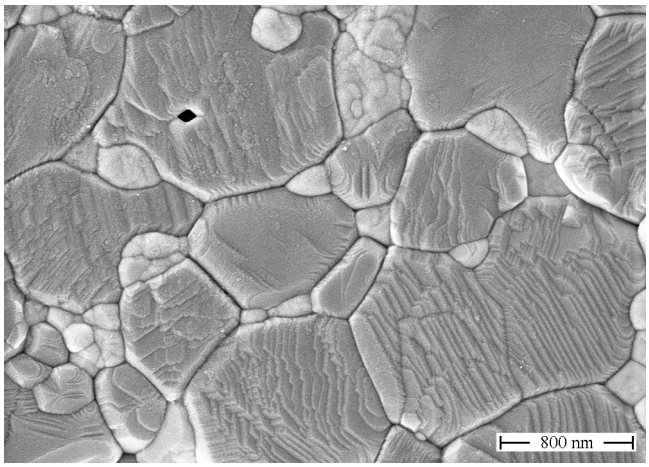

Fig. 1 a: Microstructure of injection-molded unstabilized ZTA-10 pressureless sintered at 1500 °C/2 h, thermally etched 1350°/0.5 h.

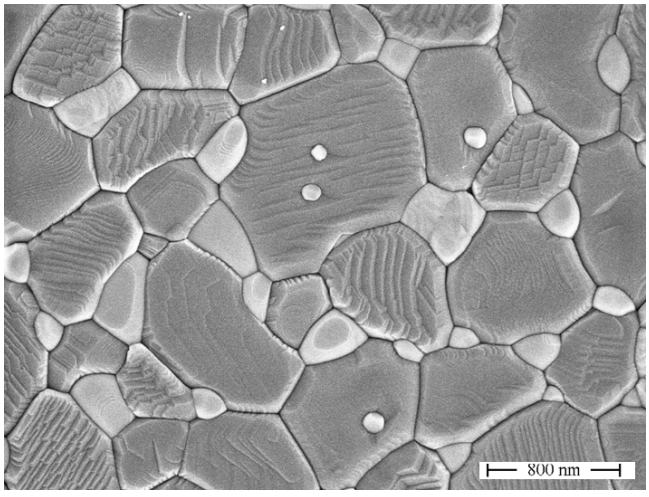

Fig. 1 b: Microstructure of hot-pressed unstabilized ZTA-10 sintered at 1500 °C/2 h/60 MPa, thermally etched 1350°/0.5 h.

The injection-molded and hot-pressed ground and polished ZTA samples were aged for 6, 12, 24 and 48 h as a simulation for its behavior *in vivo*. The monoclinic phase volume fractions of injection-molded and hot-pressed ZTA during ageing at 134 °C in an autoclave are shown in Figs. 2 and 3 respectively. In both cases the monoclinic fraction rises with time and decreasing stabilizer content. As known from literature some samples – probably owing to cooling stress – contain up to 20 % of monoclinic right from the start [14]. This initial monoclinic content is generally higher for the injection-molded samples. Addition of stabilizer reduces the initial monoclinic content. Ageing generally proceeds faster in injection-molded materials. This is probably related to their lower density. This low density has two aspects A certain amount of porosity, es-

pecially open porosity, facilitates the intrusion of water. A less dense structure leads to a lower Young's modulus and thus changes the transformation characteristics. As phase transformation is associated with volume expansion, a rigid matrix will counteract transformation. Elastic properties are correlated to density, so more transformation is expected in the less dense and rigid injection-molded samples. During the autoclave treatment the water vapor may diffuse into the imperfectly densified structure and gain access to zirconia grains below the surface. If these grains are easily transformable as in case of the unstabilized ZTA the material structure can be subverted. As shown in the results, the transformability of zirconia rises gradually as the stabilizer content decreases. Unstabilized injection-molded ZTA (IM ZTA-0Y) exhibited a very fast transformation rate at the surface achieving a monoclinic fraction of 68 % after 6 h of ageing owing to the ease of water diffusion into the bulk material and consequently, transforming the surrounding t-ZrO_2 grains. Further ageing of injection-molded unstabilized ZTA to 48 h in an autoclave increased the monoclinic fraction up to 75 %. The very fast drop in Young's modulus during ageing of IM-ZTA-0Y (Fig. 8) is a clear identification of microcracks forming in the matrix, once this process begins a self-reinforcing process of microcracking and transformation proceeds which comes to an end only when nearly all tetragonal zirconia is eliminated.

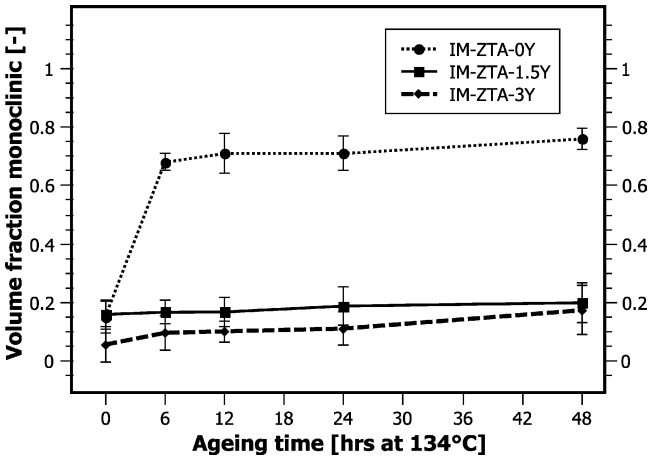

Fig. 2: Monoclinic fraction of injection-molded ZTA vs. ageing time.

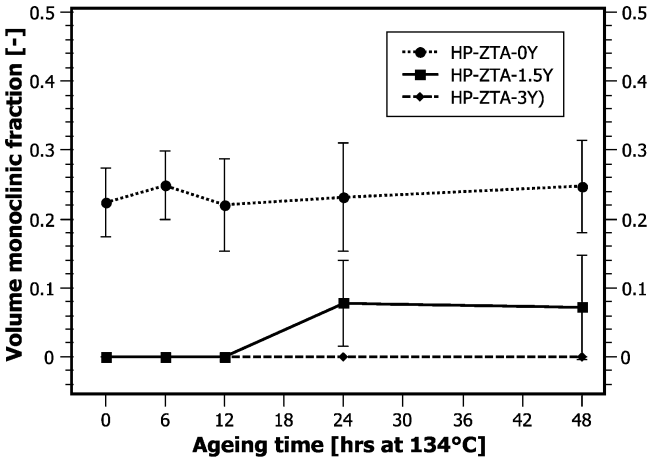

Fig. 3: Monoclinic fraction of hot-pressed ZTA vs. ageing time.

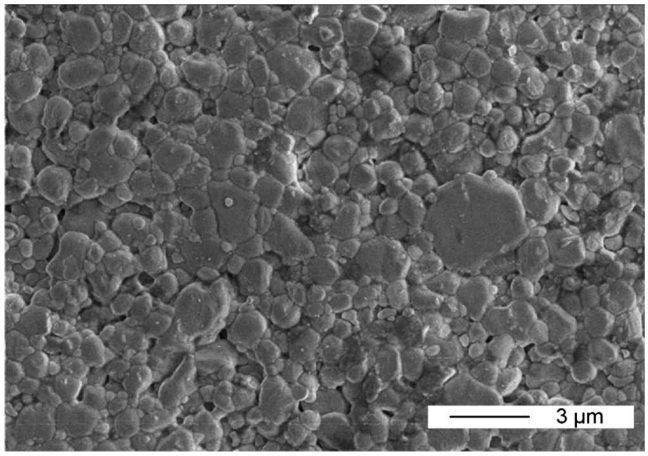

Fig. 4: Microstructure of 48-h-aged injection-molded unstabilized ZTA-10 pressureless-sintered at 1500 °C/1 h, thermally etched 1350°/0.5 h.

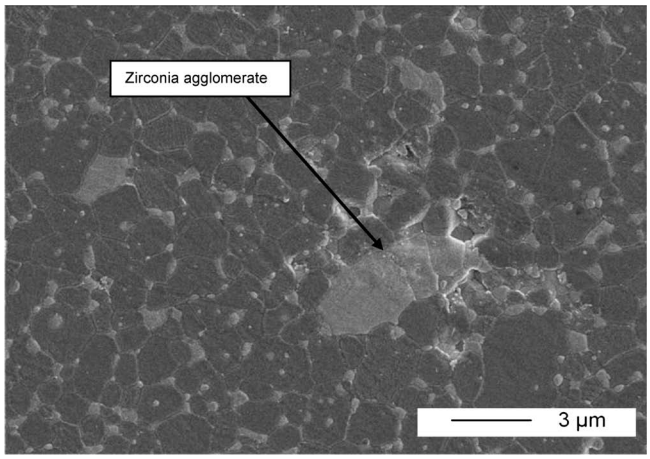

Fig. 5: Microstructure of 48 h-aged hot-pressed unstabilized ZTA-10 pressureless-sintered at 1500 °C/1 h, thermally etched 1350°/0.5 h.

The IM ZTA-0Y, IM ZTA-1.5Y and IM ZTA-3Y samples before and after 48 h of ageing at 134 °C in autoclave were cross-sectioned using a Struers Accutom 50 cutting machine at a cutting speed of 0.005 mm/s. The cross-sections were manually polished and the monoclinic phase fractions before and after ageing were determined as previously discussed. The monoclinic phase fractions at the cross-sections are similar to the fractions determined previously on the surface, which is in accord with the interpretation postulating open porosity, in fact in density measurements using ASTM C20 – 00 method an amount of open porosity of 0.3 – 1.5 % was identified.

Deville *et al.* has also reported a monoclinic fraction of 80 % in unstabilized 15 wt% ZTA processed with the powder mixing route after 120 h ageing [20]. We can observe that the monoclinic fraction of the hot-pressed unstabilized ZTA (22 – 25 %) remains almost unchanged during the ageing treatment (Fig. 3). The velocity of ageing can thus not be correlated to grain size nor to stabilizer content, which are almost identical. During ageing of HP-ZTA-0Y we only observe a slight decrease in Young's modulus, which proves that the microcrack formation is much less severe, and – if significant at all – limited to the surface area, while owing to the porosity of IM-ZTA-0Y the damage may affect the bulk. As elastic properties were

measured by micro-indentation $HV_{0.1}$ with a penetration depth of < 2 μm this interpretation remains speculative. The observed – definitely monoclinic – zirconia aggregates up to 3 μm in size in HP-ZTA-0Y seem to have little effect on ageing resistance as the vast majority of grains have a size similar to those in the injection-molded material.

The influence of ageing on the monoclinic phase content was improved by increasing the stabilizer content. Injection-molded samples were able to retain 80 % and 83 % of the t-ZrO_2 phase after 48 h of ageing at 1.5 mol% and 3 mol% yttria content respectively.

On the other hand, the transformability of zirconia in the hot-pressed ZTA containing 1.5 mol% yttria was only triggered after 12 h of ageing. A monoclinic fraction of 7 % was observed after 24 h of ageing and no further transformation was detected upon additional ageing. The hot-pressed ZTA containing 3 mol% yttria was completely stabilized and was not affected at all by ageing.

Of course, overstabilizing the ZTA is not the solution and leads to the concept of ZTA *"ad absurdum"*. It can severely corrupt strength and toughness. Overstabilized zirconia grains are not only stable against low-temperature degradation but also against stress-induced transformation converting the effect of the zirconia to a pure dispersion toughening with little beneficial effect.

However, in the case of IM-ZTA which is not completely dense, an addition of yttria is not as detrimental to the mechanical properties as to fully dense materials. On the contrary, we may state that at the given composition of 10 vol% zirconia a certain amount of stabilizer – probably less than 1.5 mol% – may not only be tolerated but is necessary to keep the material from degrading.

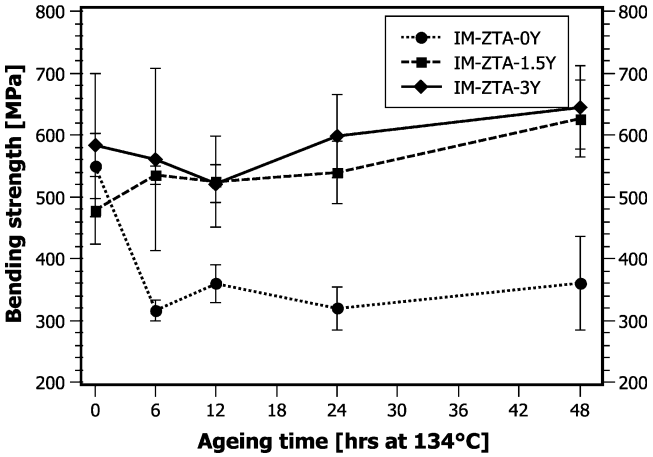

Fig. 6: The bending strength of injection-molded ZTA at different stabilizer content vs. ageing time.

The bending strength of stabilized and unstabilized injection-molded ZTA is show in Fig. 6 as a function ageing time. The bending strength of stabilized ZTA exhibits a clear trend to increase gradually with ageing time, attaining over 600 MPa after 48 h of ageing. On the other hand, the strength of unstabilized ZTA decreased sharply from 550 to 320 MPa after 6 h of ageing. The measurements confirm that, as in case of the stabilized ZTA, a slight transformation of surface-near zirconia can introduce compressive stress and enhance mechanical properties. For the same reason transformation-toughened materials like ZTA or Mg-PSZ are often used in as-ground and thus pre-stressed state. The example of IM-ZTA-0Y shows, however, that this level of pre-stressing has to be carefully adjusted and should not be excessive.

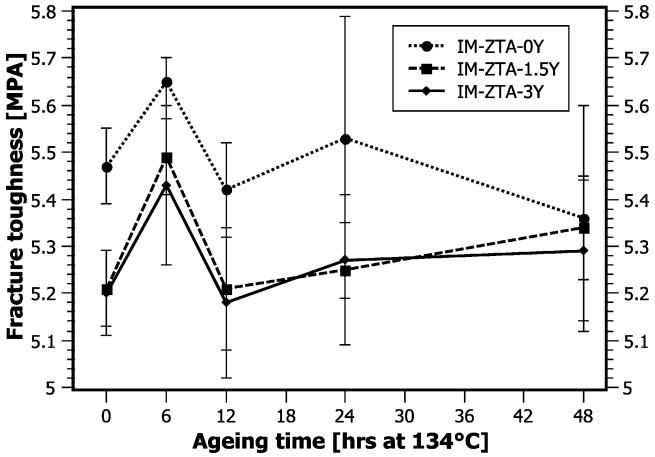

Fig. 7: Indentation fracture toughness of injection-molded ZTA at different stabilizer content vs. ageing time.

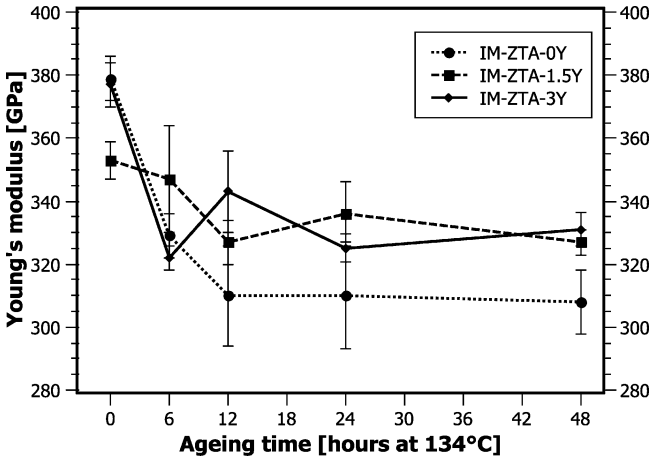

Fig. 8: Young's modulus of injection-molded ZTA at different stabilizer content vs. ageing time.

The decrease in strength is attributed to the formation of microcracks due to t-ZrO_2 transformation which is accompanied by volume expansion. Probably the formation of microcracks has also increased the fracture toughness of unstabilized ZTA after short ageing as shown in Fig. 7. Further ageing of unstabilized ZTA increases the transformation of t-ZrO_2 and leads to the formation of microcrack networks and the loss of structural integrity. The trend of fracture toughness in respect of the ageing time of both ZTAs is similar, however, hot-pressed ZTA always achieved a higher value in comparison to injection molding. Fracture toughness of 5.8 and 5.34 MPa·√m for hot-pressed and injection-molded ZTA-0Y after 48 h of ageing were approached respectively. The higher toughness may be at least partly an artifact of the measurement as the Niihara formula gives a "bonus" to harder and stiffer materials. Based on the toughness measurement by indentation alone these assumptions are somewhat speculative as the measured toughness is only a surface property. Taking into account the strength measurements, we observe a positive strength toughness correlation for the stabilized samples but an inverse correlation for the material without stabilizer. At similar toughness level a decrease in strength indicates an increase in the critical flaw size, which may be related to a network of microcracks. As expected, the

hardness (Fig. 9) of the injection-molded ZTA decreases as a function of the ageing time. In contrast, the hot-pressed ZTA only shows a slight decrease in hardness (not shown).

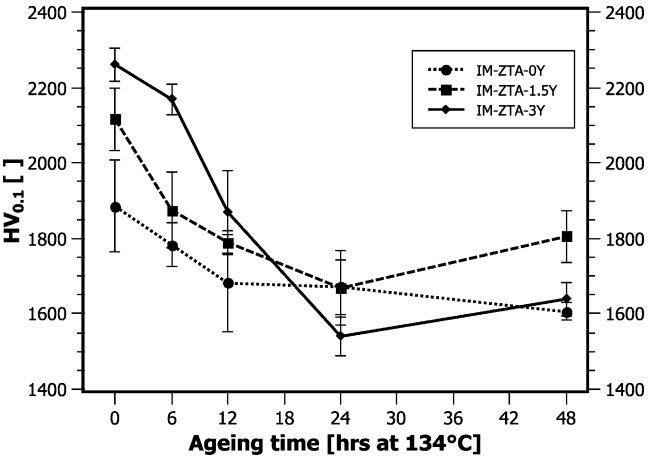

Fig. 9: Micro-hardness $HV_{0.1}$ of injection-molded ZTA at different stabilizer content vs. ageing time.

IV. Conclusion

The ageing resistance of ZTA is influenced by stabilizer content, processing and ageing time. The mechanical properties of ZTA are influenced by ageing and the ageing behavior of hot-pressed ZTA is generally slower than for injection-molded ZTA. The incomplete densification of injection-molded ZTA during pressureless sintering facilitates the penetration of water into the bulk material, resulting in ageing not just of the surface. The results showed that 1.5 mol% yttria was required in the injection-molded ZTA to retain 80 % of the t-ZrO_2 phase after 48 h of ageing. In contrast, the hot-pressed unstabilized ZTA after the same time was able to retain 75 % of the t-ZrO_2. The bending strength of yttria-stabilized injection-molded ZTA exceeded 600 MPa after severe ageing. On the contrary, the strength of the unstabilized injection-molded ZTA decreases quickly to 300 MPa after a short ageing time as a result of microcracking. The hardness and Young's modulus of the unstabilized ZTA manufactured by means of injection molding and hot pressing were found to be inversely proportional to ageing time. A good zirconia dispersion in injection-molded ZTA was achieved. It will be worth testing the improvement of ageing behavior and mechanical properties based on additional post-HIPing. This will require complete elimination of open porosity with a higher pre-firing temperature or longer dwell.

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