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Mechanical properties of alumina infiltrated zirconia nanocomposites

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ABSTRACT

In the last 20 years, great interest has been directed to alumina-zirconia composites, either in materials with low zirconia content (zirconia-toughened alumina, ZTA) or with low alumina content (alumina-toughened zirconia, ATZ). In these ceramics, the aim is to combine the large hardness of alumina with the high toughness of zirconia in order to design composites with tailored properties.

In this work, a study of ATZ is carried out by producing the composite with a simple method based on infiltration of pre-sintered zirconia porous blanks with a solution containing Aluminum nitrate salts. This process is followed by drying and sintering. The final alumina distribution and volume fraction is analyzed on the surface after cyclic infiltration. Mechanical and degradation properties of composites have been studied for different alumina contents, observing higher resistance to hydrothermal degradation and indentation fracture toughness when comparing these materials to standard 3Y-TZP.

1. INTRODUCTION

Zirconia based ceramics have been widely used since the 80's as structural materials, especially in the biomedical field for joint arthoplasty and dental restorations. This success can be explained by the good mechanical properties in terms of fracture toughness, strength and wear behavior, together with biocompatibility, offered by those materials [1], [2]. These properties are justified in part as a result of the transformation toughening mechanism: when a tailored amount of stabilizer is added to pure zirconia (usually 3 mol% of yttria to form Tetragonal Zirconia Polycrystals, 3Y-TZP), the tetragonal phase, normally stable above 1170 ºC, can be retained at room temperature in a metastable state. The transformation into the stable monoclinic phase, accompanied by a volume expansion of approx. 5 %, can be triggered by high local tensile stresses. When this occurs ahead of a growing crack, the tetragonal-to-monoclinic (*t-m*) transformation helps in arresting crack propagation, resulting in a fracture toughness increase [3], [4].

Nonetheless, after the failure of some 3Y-TZP femoral heads in 2001, it was confirmed that tetragonal zirconia suffers of the so-called Low Temperature Degradation (LTD or aging) even at human body temperature. In this phenomenon, which occurs when the material is exposed to humid environment and moderate temperatures, the *t-m* transformation occurs spontaneously and progressively with time starting from the surface of the device [5]. The local volume change results in surface roughening, grain pull-out and micro-cracking, with an important loss in contact mechanical properties [6], [7]. These evidences have raised a lot of concerns about the safety of zirconia and limited its employment in many countries [8]; on the other hand, lot of effort has been directed to the improvement of zirconia aging properties and to the design of new zirconia based composites. The most promising solutions are represented, up to now, by zirconia-alumina composites, which have been developed mostly in the low yttria content region, *i.e.* Zirconia Toughened Alumina (ZTA), [9]. In these materials, the higher hardness and absence of aging offered by alumina are combined with the toughening effect promoted by the addition of around 20 vol% of TZP. Nevertheless,

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ZTA has to be sintered at higher temperatures and with multiple steps. Alumina Toughened Zirconia (ATZ), where zirconia is the main phase, has also been studied [10], [11] and currently some companies are producing materials based on this concept (Metoxit AG, Switzerland and Mathys Orthopädie GmbH, Germany, among others), since they have shown to be less susceptible to LTD and wear. ATZ with different alumina contents have been developed using different techniques, including co-precipitation of the powders, milling and/or mixing of the compounds, coating of zirconia powder with alumina precipitated from a precursor solution and infiltration of porous ziorconia performs with molten Aluminum Nitrate salts [12-16].

In this work, ATZ is prepared through the infiltration of pre-sintered porous yttria-stabilized zirconia preforms with an aqueous solution of Aluminum Nitrate Nonahydrate, followed by drying, salt decomposition and sintering. The infiltration step is very simple and easy to include inside common zirconia manufacturing processes, after CAD/CAM shaping. The effect of alumina addition is studied in terms of microstructure, hardness, indentation fracture toughness and aging behavior. Different alumina contents are obtained through cyclic infiltration and then tested.

2. MATERIALS AND METHODS

2.1 Material preparation
The base material was TZ-3YSB-E powder provided by Tosoh Corporation, compacted by isostatic pressing at 200 MPa with a dwell time of 10 minutes. The rod-shaped green bodies of 80 x 10 mm were pre-sintered at 1100 °C and cut into discs of approx. 2 mm thickness. Density and apparent porosity were measured with the Archimedes' method. Four materials were produced. The reference material, named "AS", was sintered in air at 1450 °C, with a 2 hours dwell time and heating/cooling rates of 3 °C/min. In the porous discs corresponding to the other three conditions, the infiltration procedure was applied: first, they were dipped into a saturated solution of Aluminum Nitrate Nonahydrate ($Al(NO_3)_3$-$9H_2O$, Panreac) in distilled water during 2 hours to ensure infiltration in the open porosity. The solution in excess was eliminated from the surface with dry paper and the discs were first dried at 100 °C for 1 hour, then the temperature was raised slowly up to 400 °C to allow the decomposition of the salts into aluminum oxide, with a dwell time of one hour. The decomposition temperature was chosen based on DTA/TGA results reported elsewhere [17]. The infiltration/decomposition process was repeated 1, 2 and 3 times to obtain the materials named, respectively, "ATZ-1", "ATZ-2" and "ATZ-3". The sintering was carried out similarly to the AS material, maintaining the typical zirconia firing temperature of 1450 °C.

2.2. Microstructural characterization
Polished samples were thermally etched at 1350 °C for 1 h, and FE–SEM images (Zeiss Neon 40) were obtained from the external surfaces. The average grain size was calculated using commercial image processing software (ImageJ, USA) and the linear intercept method, with no correction factor [18]. At the same time, the volume fraction of alumina grains was estimated.

2.3. Aging behaviour
Simulated degradation was carried out on the indented samples under water vapor at 131 °C and 2 bar during 30 h. According to the degradation kinetics studied in 3Y-TZP by other authors [19], every hour of the accelerated treatment corresponds roughly to 4 years at body temperature and atmospheric pressure. In order to compare the resistance to degradation of the various materials, XRD analysis was performed on the polished surfaces of the degraded samples using a Bruker AXS D8 Advance diffractometer with Cu-Kα (1.5406 Å) radiation and symmetric $\theta/2\theta$ configuration. The equation proposed by Toraya et al. [20] was employed to calculate the monoclinic phase content and so the aging sensitivity.

2.4. Mechanical properties
Hardness was determined from Vickers indentations with loads of 0,5 Kg and 1 Kg performed with a micro-indenter (Akashi) on the polished surface of discs. Indentation fracture toughness was estimated from the length of the indentation cracks originated from 10 Kg Vickers indentations. In this case, K_{IC} was evaluated using the formula proposed by Niihara [21].

3. RESULTS AND DISCUSSION

After pre-sintering, the measured density was 52.0 ± 0.2 % of the theoretical one, with an apparent porosity of 47.0 ± 0.4 %. After sintering, the density was 6.07 ± 0.02 gr/cm^3 for the AS material, reaching almost the theoretical value.

The four microstructures obtained are represented in Figure 1, while the average grain size, HV0,5 hardness and the estimated Alumina volume fraction are summarized in Table 1.
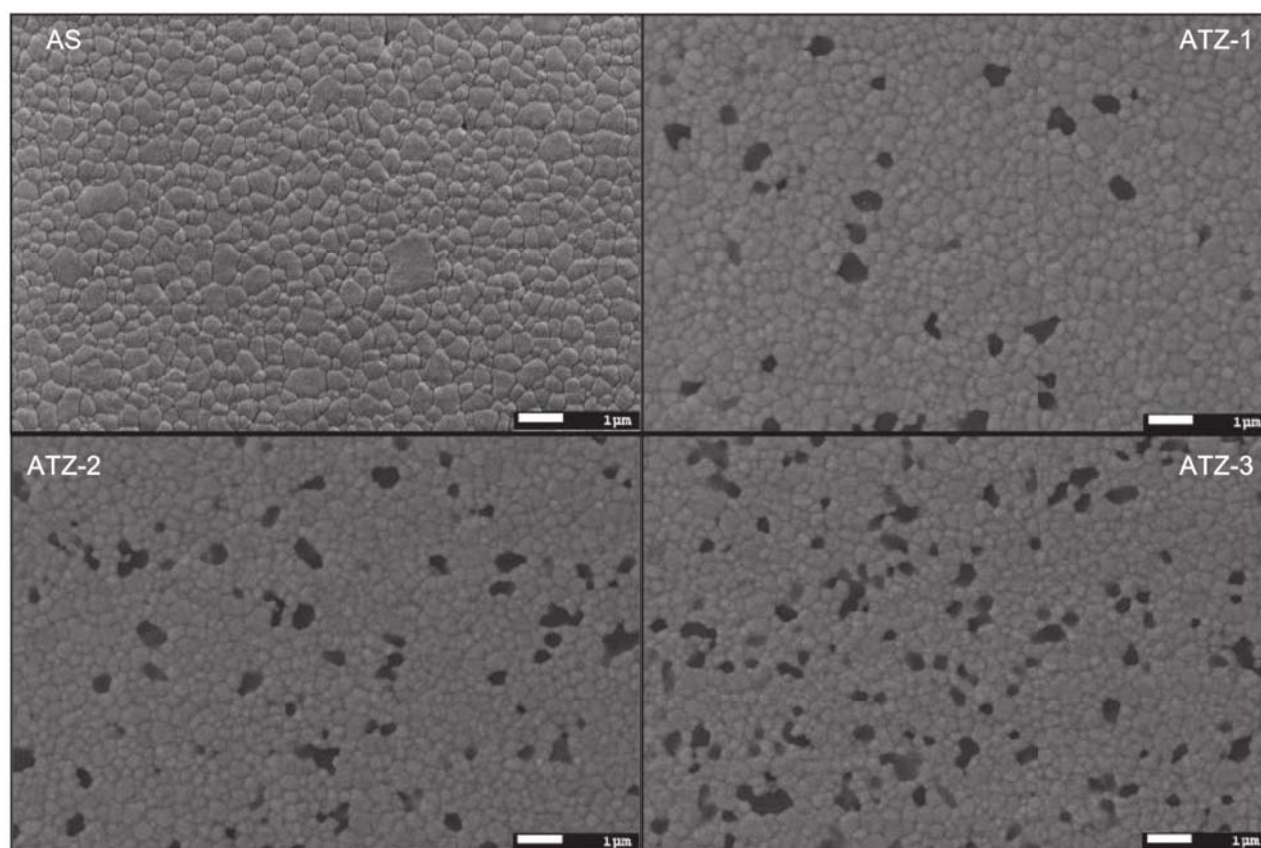

Figure 1. FE-SEM micrographs of the AS , ATZ-1, ATZ-2, ATZ-3 microstructures. Alumina grains con be recognized by darker color. Scale bar = 1 μm.

Table 1. Average grain size, hardness and alumina volume fraction of the four materials tested

Condition	AS	ATZ-1	ATZ-2	ATZ-3
Av. grain size (μm)	0.37	0.35	0.32	0.31
HV0.5 (GPa)	13.2±0.1	14.1±0.2	14.7±0.4	15.4±0.6
Alumina V_f (%)	0	4	6	10

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Micrographs show that, after cyclic infiltration/decomposition procedure, higher amounts of alumina are added, up to 10% V_f for 3 infiltrations. In the same way, zirconia grain size is reduced from 0.37 μm of the reference material to 0.31 μm of ATZ-3. This is probably imputable to grain boundary pinning effect promoted by alumina [13], [22].
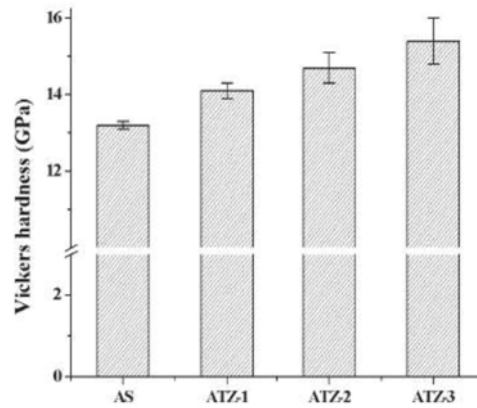

Figure 2. HV0,5 hardness of the AS , ATZ-1, ATZ-2, ATZ-3 materials.

As shown in Figure 2, Vickers hardness increases with the alumina content. There are two reasons for this behavior: on the one hand, alumina grains are harder (18 GPa approx.), and the overall hardness should be the result of averaging the hardness of the two components by their volume fraction. On the other hand, the reduction of the grain size registered in zirconia grains is responsible for a further hardness increase.
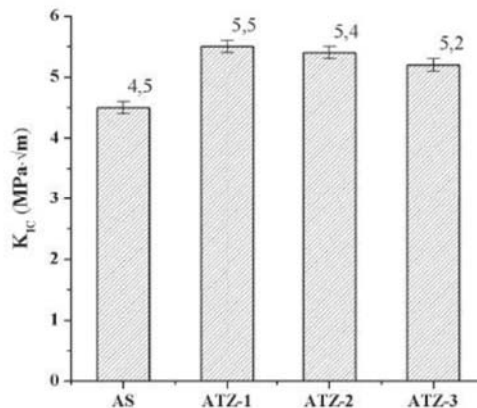

Figure 3. Indentation fracture toughness of the AS, ATZ-1, ATZ-2, ATZ-3 materials.

Indentation fracture toughness was increased from 4.5 to 5.5 MPa·√m by alumina addition through one infiltration process. Nevertheless, cyclic infiltrations seem to not allow any further increase. The fracture toughness measured by the indentation method is directly connected to the length of the cracks produced by residual stresses introduced with the indenter penetration into the surface. In the case of composite materials, where constituents have different properties, other residual stresses can be generated and sum up to the formers, producing a different crack length and apparent K_{IC} value. In the present case, crack deflection mechanisms are not likely to take place due to the sub-micrometric size of both alumina and zirconia grains. Thermal residual stresses are likely to be introduced after firing due to the different thermal expansion coefficients of alumina and zirconia (approx. 8 and 10 X 10^{-6} °C^{-1}, respectively). The thermal expansion mismatch produces a local stress state where alumina is compressed by surrounding zirconia grains, while

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the latter are in compression in the radial direction and in tension tangentially. The overall sum of the stress in zirconia must be positive, in order to compensate the negative stresses into alumina grains and guarantee static equilibrium. Considering this scenario, one can imagine that zirconia grains in contact with the second phase are locally destabilized and more transformable, resulting in an increased transformation toughening effect and higher K_{IC}. On the other side, tensile stresses inside zirconia could also contribute to crack propagation, so the measured value is the result of the sum of this opposed phenomena. Low alumina contents seem to be enough to produce a fracture toughness increase, while with further additions the two phenomena appear to compensate each other. Moreover, the smaller grain size measured in ATZ-2 and ATZ-3, contributes in stabilizing zirconia tetragonal phase, lowering therefore toughening mechanism.
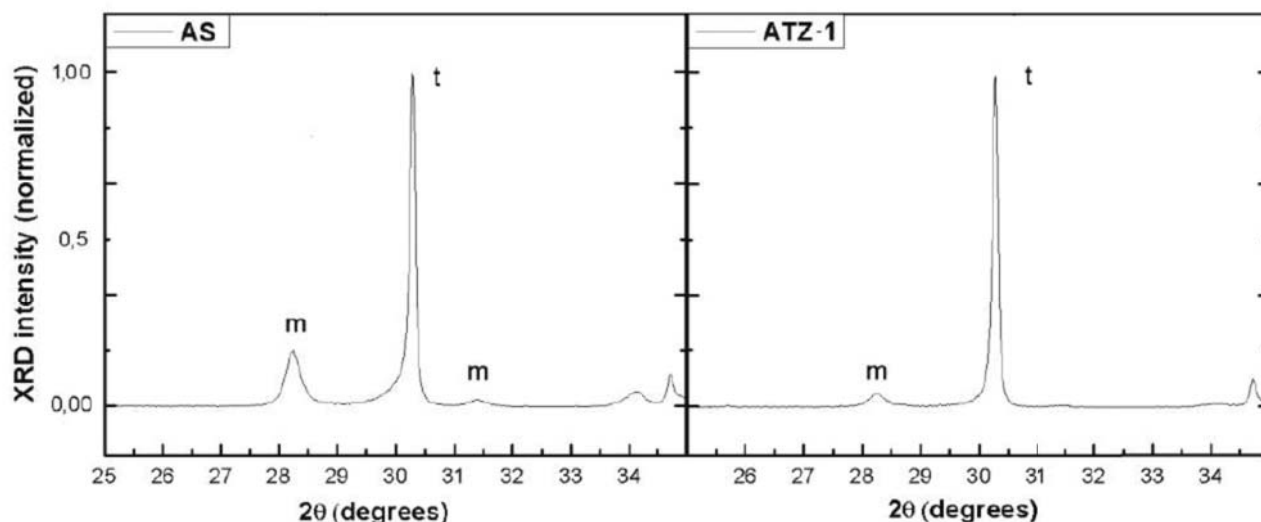

Figure 4. DRX patterns of AS and ATZ-1 materials. Tetragonal and monoclinic peaks are indicated with *t* and *m*, respectively.

Aging resistance was increased in ATZ-1 with respect to the reference material. One possible explanation is given by the smaller zirconia grain size obtained with alumina addition. Aging behavior is directly related with zirconia grain size, being the material with smaller grains less susceptible to LTD [4]. Another point to take into account is that high stiffness alumina grains could arrest zirconia grain transformation constraining mechanically the volume change. Furthermore, various authors reported that alumina impurities at grain boundaries help against hydrothermal degradation and that Al_2O_3 may suffer hydroxylation in contact with water giving similar effects [23].

4. CONCLUSIONS

ATZ nanocomposites have been developed using the nitrate infiltration method into zirconia porous blanks. Alumina volume fractions of 4, 6, and 10% have been achieved with cyclic infiltration/decomposition.
Vickers microhardness was increased with the alumina content up to 15.4 GPa for 10% V_f. Indentation fracture toughness was significantly increased with one infiltration, while no further increase was registered after repeating the process 2 and 3 times. The increase in toughness is explained through the local destabilization of zirconia grains around the ones of alumina, in which tensile stresses are introduced after sintering due to thermal expansion mismatch. The reason for no further toughness increase with greater alumina content may be due to the compensation of the destabilization mechanism caused by the lower grain size obtained and higher residual tensile stresses. The latter could be added to indentation residual stresses and contribute to crack propagation.
Hydrothermal degradation was slightly reduced in ATZ after accelerated aging. This is possibly due to the lower grain size obtained, mechanical stabilization against volume change, presence of alumina impurities at grain boundaries and alumina hydroxylation in contact with water.

5. ACKNOWLEDGMENTS

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