Influence of relative humidity and low temperature hydrothermal degradation on fretting wear of Y-TZP dental ceramics

Amparo Borrell^{1*}, Lorena Gil¹, Alvaro Presenda¹, Maria D. Salvador¹, Jozef Vleugels², Rodrigo Moreno³

¹Instituto de Tecnología de Materiales (ITM), Universitat Politècnica de València (UPV), Camino de Vera s/n, 46022, Valencia, Spain

²Department of Materials Engineering (MTM), KU Leuven, Leuven, Belgium

³Instituto de Cerámica y Vidrio (ICV), Consejo Superior de Investigaciones Científicas (CSIC), E-28049 Madrid, Spain

**Corresponding author at:* Instituto de Tecnología de Materiales (ITM), Universitat Politècnica de València, Camino de Vera s/n, 46022, Valencia, Spain. Tel.: + 34 963 877 000. aborrell@upv.es (A. Borrell)

ABSTRACT

Dental pieces are subjected to constant friction due to grinding during mastication and mouth disorders such as bruxism. Therefore, wear resistance of Y-TZP materials used for dental prostheses must be investigated. In this work, the influence of humidity and low temperature hydrothermal degradation (LTD) in 3Y-TZP ceramics subjected to fretting has been evaluated. A 100% r.h. reduces the effects of wear due to the lubricative effect of water, compared to those at ambient r.h. COF, wear volume and damage are considerably lowered at a r.h. of 100%. Exposure to degradation conditions for 25 h increased the vulnerability to wear damage of LAVA grade Y-TZP sintered at 1400 °C since the critical grain size of 300 nm was exceeded.

Keywords: Y-TZP; Humidity; Low temperature degradation; Fretting

1 Introduction

Yttria-stabilized zirconia polycrystalline (Y-TZP) ceramics possess unique properties that make them suitable for tribological applications, such as high resistance to wear, high hardness and, particularly, a high fracture toughness compared to other ceramic materials, as well as high resistance to plastic deformation, high compressive strength and thermal and chemical stability [1–3]. Among some of their most important engineering applications are their implementation as structural elements for replacement of biological systems in the human body as hip joint implants and dental prostheses. For odontological applications, zirconia materials have been widely accepted due to their mechanical, chemical and aesthetic properties. However, more

information is required regarding their wear behavior while performing under highly humid environments, which is the case of the oral cavity, and the effects that low temperature hydrothermal degradation (LTD) might produce, a phenomenon known to cause spontaneous 'ageing' and loss of mechanical properties in this material.

During mastication and in mouth disorders such as bruxism, teeth experience constant contact and small tangential displacements between surfaces at varying loads. If a synthetic material, such as zirconia, is set to act as replacement of a dental piece, these factors need to be considered. Fretting wear is a special case of sliding motion that deals with the repetitive sliding surface contact at low amplitudes, usually within a range of a few hundred micrometers [4]. Radial and linear fretting wear can be applied to describe wear on dental systems due to the nature of the contact [5]. In linear mode fretting wear, a tangential displacement between contacting surfaces occurs causing tangential friction forces to increase substantially. Radial mode consists of a perpendicular contact between surfaces where a normal force is applied in a repetitive manner [6,7]. From this two, linear mode results in a higher rate of material removal due to the nature of the contact and the friction forces that arise during sliding. The effects of linear fretting wear can be notably observed during grinding. For this purpose, a ball-on-plate setup in linear mode has been considered in this work. In fretting, three main contact regimes have been identified: stick, partial slip and gross slip. These regimes are based on the elastic and plastic deformations involved as a consequence of the contact between surfaces. Wear damage depends on the regime that arises from the applied conditions, such as load, displacement and frequency, being the stick regime the one with least damage and gross slip the one with the most damage. Different wear mechanisms can be found in each regime and, therefore, this idea needs to be considered when assessing the effects of external factors on fretting.

In order to better describe the interaction between contacting surfaces of artificial teeth elements, the effects of humidity need to be addressed. Several authors have described the most important differences in fretting wear of Y-TZP systems under low, ambient and high humidity conditions [8–10]. Highly humid environments significantly reduce the wear rates of self-mated zirconia materials due to the lubricative effect of water, while low humidity atmospheres significantly increase the volume removed due to fretting wear. The relative humidity levels in the oral cavity are constantly around 100%. Hence, the necessity to investigate the wear mechanisms involved under fretting of commercial dental materials under very high relative humidity conditions has become an important topic in the last few decades.

Another relevant aspect to consider in humid environments are the effects of low temperature hydrothermal degradation (LTD) that affects Y-TZP materials. LTD occurs as an undesired sudden transformation of tetragonal (*t*) to monoclinic (*m*) ZrO_2 due to the presence of water

[11]. Starting on the surface, LTD proceeds into the material bulk affecting the subsurface region making it more vulnerable to friction between surfaces. This spontaneous ageing phenomenon is responsible for a significant loss of the mechanical performance of these ceramics, particularly hardness and fracture toughness [12]. Additionally, the volume change associated to the *t*- to *m*-transformation results in grains being pushed towards the surface increasing its roughness [13], as well as introducing defects and microcracking in the material [14]. As a consequence, the wear behavior of Y-TZP ceramics is very likely to change. A thorough literature review indicated that no works have been found indicating the mechanisms arising from fretting of hydrothermally degraded zirconia materials.

In this sense, the purpose of this work is to evaluate the influence of humidity and LTD on the wear behavior under fretting conditions of Y-TZP dental materials. A ball-on-plate configuration has been selected in a reciprocating sliding linear mode to simulate the conditions encountered during teeth grinding. In order to assess the effects of humidity, a comparative analysis has been carried out by performing fretting tests in ambient relative humidity and 100% relative humidity environments. For assessing the influence of LTD, a previous exposure to accelerated degradation conditions were performed. These materials have been contrasted with non-degraded materials for comparison purposes. A qualitative and quantitative characterization of wear tracks including wear volume and wear track shape and dimensions has been carried out.

2 Materials and Methods

2.1 Zirconia materials

The starting two materials considered in this study are a commercial dental Y-TZP material (LAVA Zirconia, 3M ESPE, St. Paul, MN, USA), which is stabilized with 3 mol% Y_2O_3 . According to the manufacturer sheet, this zirconia material has been prepared as a co-precipitated, spray-dried powder with a particle size range between 0.07 – 0.3 μm . Samples have been cut from the pre-sintered block and shaped into 10 mm-diameter cylinders. The second one is a lab-optimized commercial zirconia powder ceramic based on TZ-3YSE (Tosoh, Tokyo, Japan). This TZ-3YSE starting powder (the average particle size is approximately 100 nm) has been dispersed by colloidal processing with the aim of optimizing the rheological behavior of the suspension in order to obtain a more homogeneous powder in terms of particle size and is finally obtained by freeze-drying. These powders were pelletized by uniaxial compression at a pressure load of 50 MPa to obtain discs with 10 mm in diameter that were used for sintering tests. Reference [15] includes specific details on the preparation of this powder. Both materials were sintered in a Thermolyne type 46100 (Thermo Fisher Scientific,

Madrid, Spain) at 1300 and 1400 °C for 2 h in air using a heating/cooling rate of 10 °C/min. For convenience, the nomenclature of the commercial LAVA and the lab-optimized ceramic are referred to as LAVA and LAB, respectively. The mechanical properties of these materials, such as hardness and Young's modulus, are reported in previous study in ref [16]. Hardness values and Young's modulus values are between 13.5-14.0 GPa and 250-270 GPa, respectively.

2.2 Fretting test setup and low temperature hydrothermal degradation (LTD)

Fretting tests have been carried out with a ball-on-plate configuration, as described in reference [17]. Zirconia balls (TZ-3Y, Tosoh, Japan) with a diameter of 10 mm and hardness of 13.2 GPa are used as counter material in all tests. The system consists of a computer-controlled tribometer where the sample to be evaluated is mounted on a translation table, which oscillates at a pre-defined frequency. The ball is fixed so that only tangential fretting wear occurs. Specimens are fixed to the sample holder that allows movement in the x and y directions. The experimental fretting parameters were kept constant for comparative reasons as follows: normal load = 8 N, frequency = 5 Hz, number of cycles = 100,000 and x direction displacement = 200 μm . These fretting conditions have been selected based on preliminary studies indicating that these conditions allow generating wear tracks of considerable size and depth within reasonable testing times.

Previous to the fretting wear tests, Y-TZP samples surface have been mirror-polished with colloidal diamond suspension down to 0.25 μm . According to Zheng et al. [18], friction and wear tests of dental components should be carried out ideally in a reciprocating sliding mode, instead of any other tribological mode, to better simulate the grinding during mastication. All tests have been carried out at room temperature.

In order to induce LTD in the sintered Y-TZP dental materials, samples were introduced in a pressurized container with distilled water at a temperature of 125 °C at 1.6 bar. An exposure time of 25 h was selected. Additionally, the LTD simulation can be easily performed and allows the investigation of the effects of zirconia ageing without having to perform in vivo experiments. It is widely utilized for studying the susceptibility of zirconia materials for dental and orthopedic applications. A comprehensive review by Pereira et al. [19] collects data of the conditions employed in several LTD-related studies to determine whether methodological parameters in autoclave influence degradation kinetics.

2.3 Tribological characterization

The dynamic coefficient of friction, COF , was calculated from the on-line measured tangential force as the average from all cycles. After fretting wear testing, the specimens were rinsed in an ultrasonic bath in ethanol for 5 min to remove any loose debris from the sample and the wear

tracks. Wear tracks were characterized to determine the wear volume and dimensions of the pit. Due to the size of the tracks, a geometrical approach was used to determine the wear volume by means of white light interferometry (Wyco NT 1100 optical profilometer, Bruker, Bellerica, USA). The measured wear pit dimensions were used to calculate the wear volume. An empirical equation modified from Klaffke [20] and reported in Reference [21] has been employed as a geometrical approximation (Equation 1). The shape of the wear track consists of an elongated round cap due to the fretting conditions applied, which means that the diameter parallel to the sliding motion, $d_{\parallel}$, is longer than the perpendicular diameter, $d_{\perp}$.

$$V = \pi h_{cap}^2 \left(R - \frac{h_{cap}}{3} \right) + \left(\frac{d_{\perp} - d_{\parallel}}{2} \right) \left[R^2 \sin \left(\frac{k}{R} \right) - (R - h_{cap})k \right] \quad (1)$$

The approach to calculate the wear volume must consider two volumes. The first one corresponds to a ball cap of height h_{cap} , which is the wear pit maximum depth. This volume corresponds to the first part of Equation 1. The second one is the portion that results from the oscillating amplitude direction. In this case, the length difference between the diameters can be used to calculate the remaining volume, which is given in the second part of Equation 1. Other parameters considered are the radius of the ball, R ($d = 10$ mm), and the factor, k , which takes into account the irregular geometrical section of the elongated side and is given in Equation 2.

$$k = \sqrt{2Rh_{cap} - h_{cap}^2} \quad (2)$$

Another important tribological parameter that can be obtained from the wear volume is the wear rate, also known as wear coefficient, which is given in Equation 3. The wear rate, W_{rate} , can be used to verify whether a gross slip regime has been reached under the selected conditions by comparing it to the fretting regimes proposed by Vingsbo et al. [22].

$$W_{rate} = \frac{V}{F_N d} \quad (3)$$

With V , the wear volume [mm^3], F_N , the normal force [N] and d , the sliding distance [m].

Qualitatively analysis of the wear track shapes was done by Nomarski microscopy (Eclipse LV 100 optical microscope, Nikon Vision Co. Ltd., Tokyo, Japan). Track features have been assessed by means of confocal microscopy with a confocal scanning laser microscope (LEXT 3100, Olympus, Tokyo, Japan). Grain size measurements to all samples were analysed by using a field emission gun scanning electron microscope images with image analysis software (FE-SEM, HITACHI S-4800, Japan). Microstructural analysis was carried out by thermally etching the samples at 100 °C below the sintering temperature. The grain size values presented correspond to the average of 50 grains measured in each sample.

3 Results and discussion

3.1 Influence of humidity on fretting wear behavior

The influence of humidity on fretting wear behavior has been assessed under highly wet environments, which is the type of conditions that dental materials are exposed to. In this case, a comparison under ambient relative humidity, (r.h 45 – 60%) and 100% r.h levels has been performed. Results of the determined coefficient of friction, *COF*, are shown in Figure 1. The analysis has been carried out with conventionally sintered materials, LAVA and LAB, for both dwell temperatures: 1300 and 1400 °C. Relative humidity has been labeled as “wet” for 100% r.h, and “dry” for ambient conditions. The relative density of LAVA and LAB materials sintered at 1300 °C is approximately between 97 and 98%, while those sintered at 1400 °C resulted in relative densities higher than 99%.

A clear pattern can be established, where *COF* for wet conditions result in lower average values. The variations in *COF* among dry specimens are less pronounced than for wet specimens, as *COF* values for wet tests range from 0.55 to 0.75, while in the case of dry values fall within 0.77 and 0.85. This means that the *COF* is reduced, in average, by 20% in wet when compared to dry. In the case of LAVA at 1400 °C, the difference is more than 30%. This pattern is in agreement with many studies that indicate that the lubricating effect of water significantly reduces the *COF* in wear fretting, particularly in ball-on-plate configurations under sliding reciprocating conditions [8,23].

Even though both materials result in a lower *COF* in the wet scenarios, LAVA shows a contrasting outcome and a bigger difference between specimens sintered at 1300 and 1400 °C. The higher dwell temperature shows a greater difference between wet and dry setups than for the lower temperature. At 1300 °C, the *COF* in the wet scenario is significantly higher than all the other wet *COF* values. This behavior differs from the dry case, where the *COF* from the higher sintering temperature is greater than at 1300 °C. On the other hand, LAB specimens show a similar *COF* in the dry case for both dwell temperatures, while those for the wet scenario reveal that *COF* increases when the temperature is increased. Moreover, the differences between wet and dry are accentuated as temperature is increased. In this case, the *COF* difference between wet and dry is more pronounced in the lower sintering temperature, contrasting with the observed pattern in LAVA.

Figure 2 show the wear track profilometric model after 100,000 cycles and Nomarski interference contrast micrographs after fretting test under wet conditions for LAVA and LAB sintered at 1300 °C (a, b, c and d, respectively), and LAB sintered at 1400 °C (e and f, respectively). The images indicate the characteristic delamination and microcracking of gross

slip are not seen. No significant material loss occurs, as only abrasive grooving in the direction parallel to sliding displacement is observed in both materials. The same behavior occurs in the 1400 °C sintered LAB material, as shown in Figure 2 (e and f).

The shape of the wear pit also differs from those obtained in dry conditions [8]. In the wet case, the tracks possess generally a higher parallel to perpendicular diameter ratio, and, consequently, appear more elongated than their dry counterparts. This change from a circular to an elliptical geometry is due to the lubricative effect of high r.h levels that decrease the COF and produce only abrasive grooving, the first stage in fretting wear. Hence, it can be established that the presence of water delays the effects of fretting wear on self-mated zirconia ceramics.

The wear scars on the counter body have also been characterized by means of optical microscopy with the aid of a multi-image capture mode due to the spherical nature of the counter material. Figure 3 shows the damage on the ball after fretting wear tests for dry and wet conditions of LAB material sintered at 1400 °C. The differences are quite significant between humidity levels and correspond to the degree of wear damage from those found in their flat counterparts. Such behavior can be attributed to the self-mating nature of the test as both materials consist of zirconia with similar properties. In the dry scenario, significant wear damage is caused by abrasive grooving and delamination leaving a rougher contact area and a wear pit diameter of approximately 600 μm . The wear scar on the ball used for fretting testing under wet conditions has a diameter half the size of its dry counterpart and the wear damage has been substantially constrained to only scratches in the sliding direction. The circular shape of these wear tracks can be attributed to the sphericity of the counter material ball. Due to the complexity of the counter material's spherical shape, white light interferometry could not be performed to obtain wear track profiles and hence wear volume has not been calculated.

The wear volume of the pits under wet conditions has been calculated with the same approach used for dry specimens. The results are given in Figure 4. A very clear pattern is observed, as wear volume loss under dry conditions is notably higher than in the case of wet. The differences correspond to more than order of magnitude between humidity conditions within each material. The surface profile of LAVA sintered at 1300 °C showed that only a rougher circular area could be observed and microscopy images indicate that the high lubricative effect of water almost completely inhibited wear damage. In the case of LAVA at the higher sintering temperature, the greatest difference between wet and dry has been observed, as a difference of two orders of magnitude has been determined. A possibility to describe this behavior are the investigations by Kleemann et al. [24]. Under atmospheric conditions, the reaction between the ceramic surface and steam will be a natural and odds-on form of lubrication. For LAB material, the wear volume decreases in the same manner for wet and dry conditions, meaning that as the sintering

temperature is increased the material resistance to wear is enhanced and less material is removed.

3.2 *Effect of LTD on resistance to fretting wear*

As no literature has been found on the fretting wear behavior of hydrothermally degraded zirconia materials, the relevance of this study relies on providing new and relevant information about this topic. In order to investigate the effect of LTD, the COF and wear volume under ambient relative humidity conditions have been evaluated in zirconia materials processed by conventional sintering at 1300 and 1400 °C and exposed to 25 h of accelerated degradation conditions. These conditions have been selected, on the one hand, based on the degradation study carried out by authors in other work [25] where *t*- to *m*-phase transformation has been detected first with Raman spectroscopy after 20 h and before 40 h of exposure. And, on the other hand, based on several studies using the relationship that 1 h of autoclave corresponds to approximately three to four years in vivo [26]. Therefore, 25 h would correspond to approximately 70-75 years, which is a realistic maximum time for a dental implant or prosthesis to be required to last.

LTD induced changes have been characterized by Raman spectroscopy to determine the presence of *m*-phase and Nomarski microscopy for evaluating the changes in surface topography resulting from phase transformation. The results for Raman spectroscopy of LAVA and LAB material sintered at 1400 °C before and after exposure to LTD are shown in Figure 5. The results of LAVA and LAB material sintered at 1300 °C before and after exposure to LTD are same to the materials sintered at 1400 °C. The spectrograms reveal the lack of *m*-phase in all specimens after 25 h of LTD exposure. Only *t*-phase peaks have been identified in both materials for both sintering conditions. If the specimens have experienced very low levels of phase transformation, these phase changes might not be revealed in the Raman spectrograms. In this case, LTD induced changes in the surface have been characterized by means of Nomarski microscopy and the images that have been obtained are shown in Figure 6. The images reveal that no significant topographical changes have occurred in LAB specimens (Figure 6d and 6h) as well as LAVA sintered at 1300 °C (Figure 6b) after 25 h of LTD exposure. However, LAVA sintered at 1400 °C (Figure 6f) results in increased surface roughness after 25 h of LTD exposure time, indicating that this specimen is particularly susceptible to phase transformation and, hence, material degradation. The need for evaluating LTD with complimentary tools have been demonstrated, as topographical analysis of the surface indicates that transformation degradation has taken place in at least one of the specimens, but Raman spectroscopy has not been able to detect such transformation.

According to the grain size results, LAVA at 1400 °C consists of the largest grain size value upon sintering (343 nm) from all the materials and sintering conditions determined in previous works [16,27]. Some studies have reported a critical particle size for *t*-stabilized zirconia ceramics in the range of 300 – 370 nm on LTD experimental data [28–30]. Exceeding this critical grain size significantly increases the susceptibility to LTD. The grain size of the other specimens does not exceed 250 nm and are therefore able to withstand the effects of LTD in a more effective manner.

Once LTD characterization has been performed, specimens have been exposed to fretting wear under ambient relative humidity conditions. The results of COF are shown in Figure 7. A direct comparison between degraded and non-degraded material after 25 h shows that variations in COF are not too pronounced, with the exception of LAVA sintered at 1300 °C. The degraded surface observed for LAVA sintered at 1400 °C in the micrograph above (Figure 6f) does not seem to influence the friction behavior, since the COF values are within the error range between degraded and non-degraded material. The pattern observed in most materials indicates that the COF of non-degraded material is greater than degraded material. However, LAB sintered at 1400 °C contrasts with this pattern. Nonetheless, the COF values fall within the error range.

The wear volume for degraded and non-degraded material under ambient relative humidity conditions has been calculated and the results are given in Figure 8. The most notable wear volume difference occurs for LAVA sintered at 1400 °C, which, according to the LTD characterization results, showed a rougher surface after 25 h of degradation exposure and higher susceptibility to this ageing phenomenon. In this case, wear volume loss is significantly reduced in the degraded material, from 1.4×10^6 to $3.1 \times 10^5 \mu\text{m}^3$. A plausible explanation for this behavior consists on the contribution of LTD to the loss of mechanical properties such as hardness and fracture toughness that increases the amount of debris generated during wear tests. A higher vulnerability to wear damage and material loss is constrained mostly to the sub-superficial zone where the *m*-phase layer has emerged. As fretting progresses, the debris accumulates and is trapped inside the wear track at the ball-plate interface and acts as a protective layer between material and counter material reducing the amount of material loss. In the case of LAB, the calculated wear volumes are not too different between degraded and non-degraded specimens, which highlights the stability of this material due to its lab-optimized nature.

Characterization of the wear tracks has been performed in a similar manner as for non-degraded material in previous sections. Surface models obtained from white light interferometry and Nomarski micrographs for LAVA and LAB sintered at 1400 °C after degradation are shown in Figure 9. A rougher surface can be observed in LAVA due to the effects of degradation. The shape of the wear track is similar to those observed in non-degraded material: an elongated

circular cap in the parallel direction to fretting displacement. The difference in measured diameters and pit depth is not too pronounced when compared to the LAB specimen, which is in agreement with the similar calculated wear volume loss between these two specimens.

The confocal microscopy images presented in Figure 10 reveal the mechanism responsible for wear damage in LAVA and LAB sintered at 1400 °C after 25 h of LTD exposure. LAB material, which appears to have not been affected by degradation, exhibits similar wear mechanisms as those found in non-degraded material, such as delamination, microcracking and abrasive grooving. In the case of LAVA, however, an interesting element has been found inside the wear track. The formation of microscopic wave-like features (pointed by the red arrow) perpendicular to the displacement direction might indicate the accumulation of debris that has accumulated and been grinded by the ball. These features have not been observed in the other degraded specimens and could be an indication of the presence of a protective layer that results from a sub-superficial loss of *m*-phase material that reduces the wear volume loss significantly.

In general, the degradation that occurs in LAVA upon sintering at 1400 °C is a consequence of the large particle size exceeding a critical value. As a consequence, the emergence of a sub-superficial *m*-phase layer can favor the generation of debris that can get trapped inside the ball and the plate and act as protective layer that reduces the overall fretting wear damage resulting in a smaller wear volume loss. Therefore, degradation can change the behavior of zirconia ceramics against fretting wear and increase resistance to material removal. More studies need to be carried out to understand the mechanism involved in the fretting wear behavior of degraded zirconia material and a more thorough understanding of the effects of LTD.

4 Conclusions

Influence of humidity on fretting wear behavior:

- The zirconia materials considered in this work under reciprocating self-mating conditions, when increasing humidity to a 100% r.h. reduces the coefficient of friction, material volume loss and wear damage effects of wear due to the lubricative effect of water contained in highly humid environments, contrasting with those of drier conditions at 45 – 60% r.h.
- From the observed wear behaviors, it can be concluded that LAB zirconia results in a more stable compared to LAVA commercial material in terms of durability and resistance to grinding for dental applications. LAVA shows significant variations in wear volume at different sintering temperatures indicating that this material is more vulnerable to processing conditions.

Effect of LTD on resistance to fretting wear:

- Exposure to LTD for 25 h demonstrated a change in the fretting wear behavior of LAVA sintered at 1400 °C. Exceeding the critical grain size of 300 nm in this specimen has increased its vulnerability to m-phase transformation. A significantly lower material volume loss compared to its non-degraded counterpart has been determined. Such behavior might be attributed to the loss of mechanical properties resulting from the emergence of a degraded sub-superficial layer that leads to a faster generation of debris. This debris is accumulated and trapped inside the wear pit as the ball presses on the plate. Consequently, a protective layer arises at the contact interface reducing the fretting wear damage.

Acknowledgements

This work has been supported by the Spanish Ministry of Economy and Competitiveness MINECO by MAT2015-67586-C3-R project and RyC contract (RYC-2016-20915), and the Generalitat Valenciana by PROMETEO/2016/040 project.

References

- [1] Clarke IC, Green DD, Pezzoti G, Donaldson D. 20 Year Experience of Zirconia Total Hip Replacements. *Bioceram. Altern. Bear. Jt. Arthroplast.*, Springer; 2005, p. 67–78.
- [2] Inokoshi M, Zhang F, De Munck J, Minakuchi S, Naert I, Vleugels J, et al. Influence of sintering conditions on low-temperature degradation of dental zirconia. *Dent Mater* 2014;30:669–78.
- [3] Piconi C, Maccauro G. Zirconia as a ceramic biomaterial. *Biomaterials* 1999;20:1–25.
- [4] Campbell PQ, Celis JP, Roos JR, Van Der Biest O. Fretting wear of selected ceramics and cermets. *Wear* 1994;174:47–56.
- [5] Basu B, Kalin M. *Tribology of Ceramics and Composites: A Materials Science Perspective*. John Wiley and Sons; 2011.
- [6] Zhu MH, Yu HY, Cai ZB, Zhou ZR. Radial fretting behaviours of dental feldspathic ceramics against different counterbodies. *Wear* 2005;259:996–1004.
- [7] Zhu MH, Yu HY, Zhou ZR. Radial fretting behaviours of dental ceramics. *Tribol Int* 2006;39:1255–61.
- [8] Basu B, Vitchev RG, Vleugels J, Celis JP, Van Der Biest O. Influence of humidity on the fretting wear of self-mated tetragonal zirconia ceramics. *Acta Mater* 2000;48:2461–71.
- [9] Basu B, Vitchev RG, Vleugels J, Celis JP, Van Der Biest O. Fretting wear of self-mated tetragonal zirconia ceramics in different humidity. *Key Eng Mater* 2001;206–213:783–6.
- [10] Krell A, Klaffke D. Effects of grain size and humidity on fretting wear in fine-grained alumina, $\text{Al}_2\text{O}_3/\text{TiC}$, and zirconia. *J Am Ceram Soc* 1996;79:1139–46.
- [11] Cattani-Lorente M, Scherrer SS, Ammann P, Jobin M, Wiskott HWA. Low temperature degradation of a Y-TZP dental ceramic. *Acta Biomater* 2011;7:858–65.

- [12] Zhang F, Vanmeensel K, Inokoshi M, Batuk M, Hadermann J, Van Meerbeek B, et al. 3Y-TZP ceramics with improved hydrothermal degradation resistance and fracture toughness. *J Eur Ceram Soc* 2014;34:2453–63.
- [13] Roy ME, Whiteside LA, Katerberg BJ, Steiger JA. Phase transformation, roughness, and microhardness of artificially aged yttria- and magnesia-stabilized zirconia femoral heads. *J Biomed Mater Res A* 2007;83:1096–102.
- [14] Lughi V, Sergo V. Low temperature degradation -aging- of zirconia: A critical review of the relevant aspects in dentistry. *Dent Mater* 2010;26:807–20.
- [15] Rayón E, Moreno R, Alcázar C, Salvador MD, Manjón FJ, Jiménez-Piqué E, et al. Enhanced hydrothermal resistance of Y-TZP ceramics through colloidal processing. *J Am Ceram Soc* 2013;96:1070–6.
- [16] Presenda A, Salvador MD, Peñaranda-Foix FL, Moreno R, Borrell A. Effect of microwave sintering on microstructure and mechanical properties in Y-TZP materials used for dental applications. *Ceram Int* 2015;41:7125–32.
- [17] Presenda A, Salvador MD, Vleugels J, Moreno R, Borrell A. Fretting fatigue wear behavior of Y-TZP dental ceramics processed by non-conventional microwave sintering. *J Am Ceram Soc* 2017;100:1842–1852.
- [18] Zheng J, Zhou Z., Zhang J, Li H, Yu H. On the friction and wear behaviour of human tooth enamel and dentin. *Wear* 2003;255:967–74.
- [19] Pereira GKR, Venturini AB, Silvestri T, Dapieve KS, Montagner AF, Soares FZM, et al. Low-temperature degradation of Y-TZP ceramics: A systematic review and meta-analysis. *J Mech Behav Biomed Mater* 2015;55:151–63.
- [20] Klaffke D. Fretting wear of ceramics. *Tribol Int* 1989;22:89–101.
- [21] Kalin M, Vižintin J. Use of equations for wear volume determination in fretting experiments. *Wear* 2000;237:39–48.
- [22] Vingsbo O, Schön J. Gross slip criteria in fretting. *Wear* 1993;162–164:347–56.
- [23] Takadom J, Houmid-Bennani H, Mairey D. The wear characteristics of silicon nitride. *J Eur Ceram Soc* 1998;18:553–6.
- [24] Kleemann J, Woydt M. Dry friction and wear rates as under liquid lubrication of ceramic/carbon couples up to 450°C. *Ind Lubric Tribol*, 2004;56: 38–51.
- [25] Presenda A, Salvador MD, Moreno R, Borrell A. Hydrothermal degradation behavior of Y-TZP ceramics sintered by non-conventional microwave technology. *J Am Ceram Soc* 2015;98:3680–9.
- [26] Chevalier J. What future for zirconia as a biomaterial? *Biomaterials* 2006;27:535–43.
- [27] Borrell A, Salvador MD, Peñaranda-Foix FL, Cálata-Civera JM. Microwave sintering of zirconia materials: mechanical and microstructural properties. *Int J Appl Ceram Technol* 2013;10:313–20.
- [28] Watanabe M, Iio S, Fukuura I. Ageing behaviour of Y-TZP. *Adv Ceram* 1984;12:391–98.
- [29] Chen SY, Lu H-Y. Low-temperature ageing map for 3 mol% Y_2O_3 - ZrO_2 . *J Mater Sci* 1989;24:453–6.
- [30] Muñoz-Saldaña J, Balmori-Ramírez H, Jaramillo-Vigueras D, Iga T, Schneider GA. Mechanical properties and low-temperature aging of tetragonal zirconia polycrystals processed by hot isostatic pressing. *J Mater Res* 2011;18:2415–26.

Figure 1. Coefficient of friction comparison between wet and dry specimens for LAVA and LAB materials sintered under two different temperatures.

Figure 2. Wear track profilometric model and Nomarski interference contrast micrographs after fretting test under wet conditions for LAVA and LAB sintered at 1300 °C (a, b, c and d, respectively), and LAB sintered at 1400 °C (e and f, respectively).

Figure 3. Micrographs of wear scars on zirconia balls employed as counter material for: a) dry and b) wet conditions corresponding to fretting tests on LAB material sintered at 1400 °C.

Figure 4. Wear volume determined for LAB and LAVA material sintered at two different temperatures under wet and dry conditions.

Figure 5. Raman spectrograms of LAVA and LAB material sintered at 1400 °C before and after exposure to LTD.

Figure 6. Surface micrographs of LAVA (a, b) and LAB (c, d) sintered at 1300 °C, and LAVA (e, f) and LAB (g, h) sintered at 1400 °C, before and after 25 h of LTD exposure.

Figure 7. COF for LAVA and LAB materials sintered at two different temperatures before and after 25 h of exposure to accelerated LTD conditions.

Figure 8. Wear volume for LAVA and LAB materials sintered at two different temperatures before and after 25 h of exposure to accelerated LTD conditions.

Figure 9. Wear track profilometric model and Nomarski interference contrast micrographs of degraded LAVA sintered at 1400 °C (a and b, respectively) and LAB sintered at 1400 °C (c and d, respectively).

Figure 10. Confocal microscopy images of the wear tracks on LAVA (a) and LAB (b) sintered at 1400 °C after 25 h of LTD exposure.

Highlights:

- Humidity and LTD significantly influence fretting wear of Y-TZP ceramics.
- High levels of humidity reduce friction and wear between flat and counter-material.
- A higher sintering temperature affects wear behavior due to grain coarsening.
- The presence of a debris layer reduced fretting damage in degraded material.