EVALUATION OF TRIBOLOGICAL PROPERTIES OF NEW ALUMINA/ZIRCONIA CERAMICS FOR DENTAL RESTORATION

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ABSTRACT
There is great interest in the use of ceramics for dental restoration due aesthetic similarity to natural teeth. Dental applications also demand adequate mechanical and tribological properties. Namely, the restoration material must not wear out easily and must not lead to abnormal enamel wear of the antagonist tooth.
In the present work ceramic composites were developed by slip casting of tailored Al_2O_3/Zr_2O formulations containing ZrO_2 in the form of submicrometric or of nanoparticles. After sintering sample surface was characterized by scanning electron microscopy and profilometry; hydrophilicity was evaluated using the sessile drop method. Wear behaviour was assessed by reciprocating pin-on-plate tests in artificial saliva, using molar and pre-molar human teeth as pins and samples of the produced materials as cusps. Commercial dental zirconia was used as reference material.
High consolidation of composites was attained, with density values ranging from 95.8 %TD to 99.9 %TD. Samples containing submicrometric zirconia present uniform reinforcement distribution and small porosity. Samples containing nanomicrometric zirconia show irregular zirconia agglomerates with micrometric dimension and higher porosity. Wear measurements show that ceramic wear is not significant, while cusps wear is strongly dependent of the opposing ceramic surface counterface roughness and porosity.
Attained results suggest that dental wear can be reduced if highly polished zirconia/alumina composites are used instead of zirconia.

KEY WORDS: Dental materials, alumina, zirconia, biotribology.

1. - INTRODUCTION
Dental restoration is used to replace missing tooth tissue after trauma or illness, aiming to re-establish the masticatory, phonetic and aesthetic functions of natural teeth. Development of new reliable and cost-effective bioceramics is thus of great significance to the dentistry community. Historically several materials have been used for the dental crowns manufacture; ceramic materials are preferred because of their aesthetic similarity to natural teeth in terms of colour and translucently. Several ceramic materials have been used, e.g. alumina, lithium disilicate and zirconia.
Dental materials must also endure the chemical, thermal and mechanical demands of the oral cavity, including wear against opposing surfaces. Dental wear is a natural and unavoidable physiological process [1,2]. However, friction between restorations

and natural teeth can introduce pathological damage of natural teeth [3]. Excessive wear leads to lack of contact between opposing teeth (or between tooth and restoration), with obliteration of chewing surfaces and disturbance of the mastication process efficiency [4]. Wear tests are thus mandatory to dismiss the possibility of tooth pathological wear, and constitute an important tool regarding selection of dental materials.
In this context the present work evaluates the tribological performance of alumina/zirconia composites and compares them with commercial zirconia used in dental crowns manufacture.

2. - MATERIALS AND METHODS

Alumina and composite alumina/zirconia plates were obtained by slip casting, using powders of alumina CT-3000-SG (Almatis, d_{50}=0,90 µm) and zirconia. Two different zirconia powders (Sigma-Aldrich) were used: submicrometric zirconia (d_{50}=0,33 µm) stabilized with 8 wt% Y_3O_2; and nanometric zirconia (d < 100 nm, according to supplier) stabilized with 3 wt% Y_3O_2.
Tailored powder mixtures were used to prepare slurries containing 70 wt% solids and 0.5 wt % dispersant (Dolapix CE64, Rohm and Haas). Four different powder mixtures were tested: 100 % alumina, and composites with 5 wt% and 26 wt%-ZrO_2. After casting the green bodies were dried in oven during 24 hours at 38 ºC. Sintering was carried out at at 1600 ºC (2 h). Obtained plates were afterwards polished to a 3 µm finish. Zirconia plates were obtained from pre-sintered zirconia blocs, which were cut and sintered according to supplier's recommendations. Part of the zirconia plates was polished to a 3 µm finish, while others were grinded to a 600 mesh finish. The notation adopted for each plate is detailed in Table 2.
The plates were characterized by roughness measurement (Mitutoyo Surftest-301). The density of sintered plates was accessed by the Archimedes method; attained values are rendered in terms of percentage of theoretical density, which was calculated by the rule of mixtures. The hydrophilicity of the plates was determined by the sessile drop method using distilled water; contact angle evolution was monitored during 1800 s using a video camera coupled to a microscope (Wild M3Z) and to a frame grabber (Data Translation DT3155). Vickers hardness of plate materials was measured (EMCO test M4U-025) using an applied load of 10 kgf and dwell time of 10 s. The hardness number was calculated based on the length of the diagonals of indentation marks, using micrographs obtained by field emission gun scanning electron microscopy (FEG-SEM) (JEOL JSM-701). Indentation toughness was calculated using the length of cracks created by the Vickers indentations using the method described by Guedes et al. [5].
The pins were prepared using molar and premolar healthy human tooth. Each tooth was cut in order to individualise its cusps, which were then mounted in acrylic resin. Before testing the cusps were immerged in distilled water to avoid sample dehydration. For each test conditions an unused cusp belonging to a different tooth was used.
Plates and cusps were observed before and after wear test by FEG-SEM coupled with energy-dispersive spectroscopy microanalysis (EDS) (Inca pentaFETx3; OXFORD INSTRUMENTS) and optical microscopy (OM) (Olympus BH2-UMA).
Reciprocating pin-on-plate wear tests were carried out in artificial saliva (pH 7) [6] using plates of the produced alumina and alumina/zirconia composites, and plates of

commercial zirconia. It should be noted that zirconia was considered in this study because of its extensive use in the dental crows manufacture. Five tests were carried out for each condition. The operational conditions used are described in Table 1.

Table 1. Wear test operational conditions.

Frequency (Hz)	1
Stroke (mm)	5
Load (N)	2
Temperature (ºC)	37
Duration (h)	6

3. - RESULTS AND DISCUSSION

Fig. 1 shows microstructural features of the produced materials after sintering.

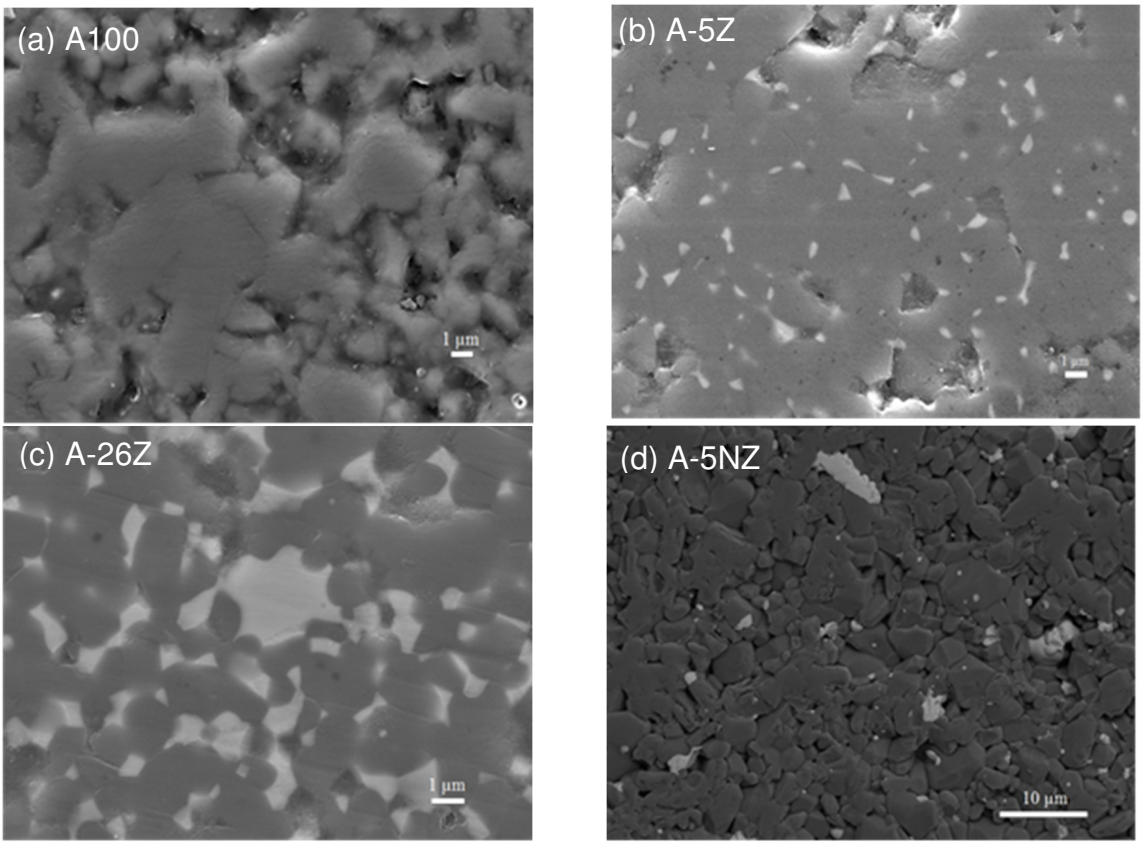

Figure 1. Backscattered electron (BSE) image of the produced materials after sintering: (a) A100; (b) A-5Z; (c) A-26Z; (d) A-5NZ (dark grey: alumina; light grey: zirconia).

Samples A100 (Fig. 1.a) and A-5NZ (Fig. 1.d) present significant porosity, in good agreement with measured density values (Table 2). The most efficient consolidation is attained for A-5Z and A-26Z (Figures 1.b and 1.c, respectively). In this samples the submicrometric zirconia reinforcement is apparently uniformly distributed within the alumina matrix, locating mainly in the matrix grain boundaries. In A-5Z the ZrO_2

phase is elongated and small, with approximately 1 μm in the longitudinal direction (Figure 1.b), which is in the size range of as-supplied particles. This suggests efficient dispersion of the zirconia phase in the prepared suspensions, and also absence of significant zirconia grain growth during sintering. In the A-26Z sample the ZrO_2 particles are bigger (up to 5 μm) and more equiaxed, suggesting grain growth during sintering. The sample containing nanomicrometric zirconia (A-5NZ) shows non-uniform reinforcement distribution (Fig. 1.d), with irregular zirconia agglomerates with dimension roughly between 1 and 10 μm located in the matrix grain boundaries. This suggests that the nanoparticle dispersion in suspension was not fully achieved, rendering heterogeneities in the course of sintering. Nanosized zirconia is visible within the alumina particles, suggesting that they become occluded during the sintering process.

The properties of the produced materials are given in Table 2. Theoretical density after sintering ranges between 95.8 % (A-5NZ) and 99.8 % (A-5Z). The low density value obtained for A-5NZ is probably due to slurry's inhomogeneous dispersion (Figure 1.d). The average roughness of the produced plates varies from 0.08 μm (Z100S) to 1.64 μm (Z100R). The contact angle value obtained for distilled water upon the produced composites is approx. 48º for A-5Z and A-26Z and 51º for A-5NZ. These values are quite similar to that of 100% alumina ($\theta \sim 55º$), and higher to that of 100% zirconia ($\theta \sim 70º$). Measured plates' hardness values range between 1200 HV (zirconia plates) and 1855 HV (A-26Z plates). Indentation toughness values of the produced materials vary between 2.9 $MPa \cdot m^{-1/2}$ for A100 (in good agreement with the theoretical value for alumina [7]) and 4.5 for A-26Z. All the alumina-zirconia samples present toughness value above that of pure alumina, suggesting that the introduction of zirconia particles contributes to alumina matrix strengthening.

Table 2. Plate identification and measured properties.

Sample identification	**Composition** (wt% ZrO_2)	**Ra** (μm)	**Contact angle** (º)	**Density** (%TD)	**Hardness** (HV10)	**K_{IC}** ($MPa \cdot m^{-1/2}$)	**Observations**
A100	0	0.22 ± 0.07	55.0 ± 3.3	98.8	1624	2.9	---
A-5Z	5	0.71 ± 0.13	47.6 ± 2.2	99.9	1789	3.5	micrometric ZrO_2
A-5NZ	5	0.28 ± 0.05	50.5 ± 3.1	95.8	----	----	nanometric ZrO_2
A-26Z	26	0.54 ± 0.22	47.9 ± 2.4	99.4	1855	4.5	micrometric ZrO_2
Z100S	100	0.08 ± 0.02	-----	----	1200 [8]	----	3 μm finish
Z100R	100	1.64 ± 052	70.0 ± 2.0	----	1200 [8]	8 [8]	600 finish

Observations of samples after wear test showed the absence of significant wear of the ceramic materials. Wear tracks could not be identified by SEM nor by surface roughness.

Dental wear was observed on all tested cusps (Fig. 2). SEM observation of the worn cusp surfaces shows a tribolayer that covers the worn area (e.g. Fig. 2.c and 2.d). This layer has granular morphology, apparently resulting from aggregation of small particles on the nanometer range. EDS microanalysis identified the presence of mainly Ca and P in all cusps, together with Zr and/or Al. These results suggest that the small particles generated during wear were adhered and compacted at the cusps surface. Tooth enamel is mainly constituted by hydroxyapatite nanocrystals, with a thickness and width of 30 mm and 60 nm, respectively, and 100 to 500 nm length [9]. The observed tribolayer is expected to result from subsurface microcraking of hydroxyapatite crystals, followed by delamination and particle compaction and agglomeration. Delamination of the tribolayer is observed (e.g. Fig. 2.d and 2.e).

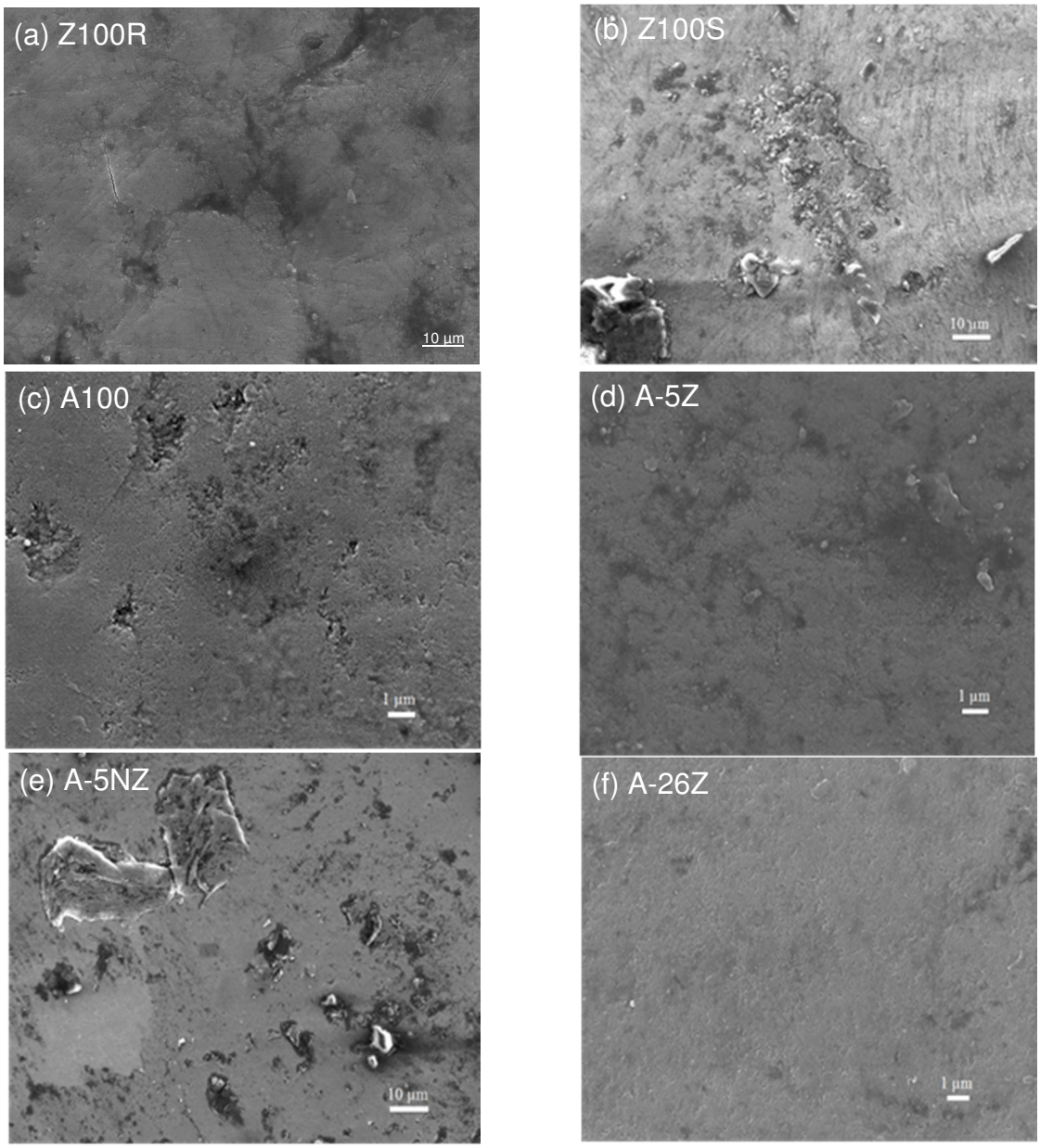

Figure 2. Secondary electron images of cusp surfaces worn against: (a) Z100R; (b) Z100S; (c) A100; (d) A-5Z; (e) A-5NZ; (f) A-26Z.

Cusps wear results are given in Figure 3. The lower wear values were obtained for cusps tested against 100% Alumina (A100) and 100% Zirconia (Z100S). The lower tribological performance of the composites can be attributed to differences in plate surface roughness values, since Fig. 3 shows that cusp wear increases with the conterface roughness. In fact, for counterfaces with the same roughness value attained results suggest that the produced composites (A-26Z and A-5Z) and 100% alumina (A100) would decrease dental wear in comparison to zirconia. More studies are needed in order to clarify this point. Higher wear was obtained for the lower consolidated sample (A-5NZ). The differences between the composites with added micro (A-5Z) and nano (A-5NZ) zirconia particles can be attributed to differences in

samples roughness (Table 2 and Fig. 1), which are suggested to outcome for the higher porosity of A-5NZ.
There is no apparent correlation between counterface hardness and the corresponding cusp wear (Table 1), showing that differences in material hardness are not the main factor in dental wear. This is in good agreement with previous results on enamel/zirconia wear by Figueiredo- Pina et al. [10].

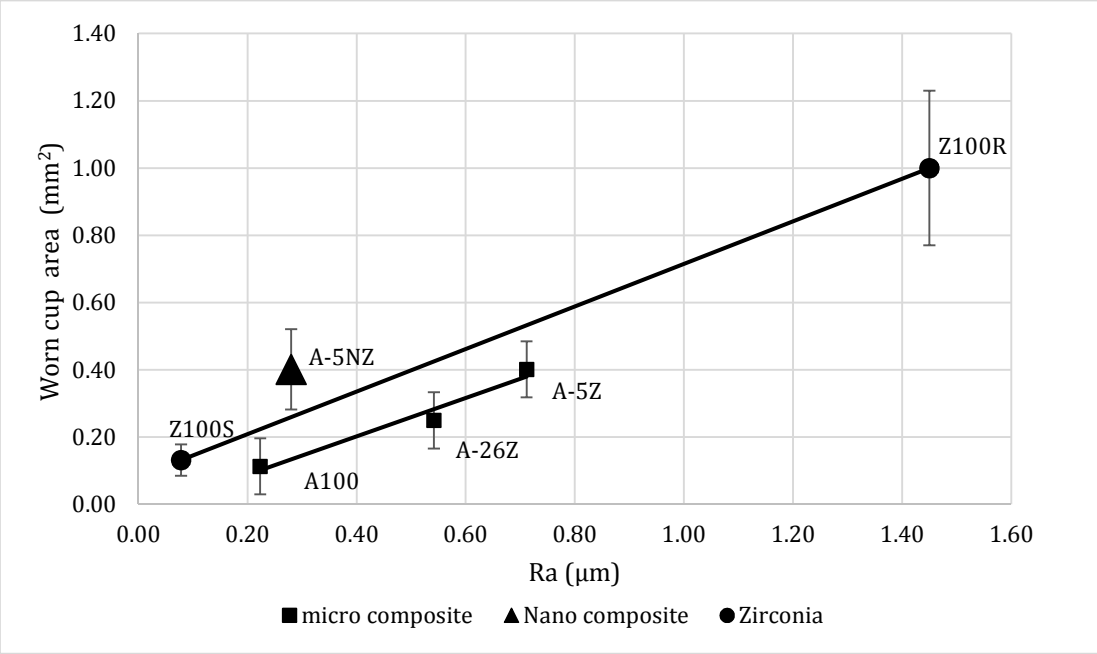

Figure 2. Correlation between worn cup area and initial plate roughness.

Attained results suggest that dental wear can be reduced if highly polished alumina or zirconia/alumina composites are used instead of zirconia. For that purpose the efficient zirconia homogenization in suspension and the reduction of porosity during the densification step of alumina and alumina/zirconia composites are mandatory.

4. - CONCLUSIONS

In order to evaluate dental wear against alumina/zirconia composites, pin-on-plate reciprocating wear tests were carried out using human molar cusps as pins in artificial saliva at 37ºC. Zirconia was used as reference material. Attained results show that:

- Dental wear is lower for the produced composites than for zirconia with the same surface conditions.
- Dental wear depends on the ceramic material densification.
- Dental wear increases with the couterface roughness.
- Apparently there is no correlation between the couterface hardness and dental wear.
- Apparently there is no correlation between counterface contact angle and dental wear.

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