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Author: Lucas Ferreira Pedrosa

Supervisor: Prof. Fernando Alberto Deométrio Rodrigues Alves Guerra, DMD, MSc, PhD

Co-supervisor: Dr. Ricardo Bernardo Dias, DMD, MSc

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Pedrosa, L.[1]; Dias, R.[2]; Guerra, F.[3]

[1] Student at the Integrated Master in Dentistry from the Faculty of Medicine – University of Coimbra, Portugal

[2] Assistant Professor of Fixed Prosthodontics at Faculty of Medicine – University of Coimbra, Portugal

[3] Associate Professor with Aggregation and Head of the Fixed Prosthodontics Department at Faculty of Medicine – University of Coimbra, Portugal

Adress:

Lucas Ferreira Pedrosa – lucas.pdrs@gmail.com

Área de Medicina Dentária da Faculdade de Medicina da Universidade de Coimbra

Av. Bissaya Barreto, Bloco de Celas, 3000-075 Coimbra, Portugal

Abstract

Objective: The aim of the present pilot study was to assess the effect of sandblasting angulations, new air abrasion powder containing zirconia, and cleaning procedure on Y-TZP ceramic surface.

Materials and Methods: A total of 4 cylindrical zirconia ceramic disks were divided in 6 different surface treatment groups and for each group 2 samples (n=2) were prepared: group 1 sandblasted with 50µm alumina powder and a 90° angulation; group 2 sandblasted with 50µm alumina powder and a 30° angulation; group 3 sandblasted with 30µm silica-coated alumina and a 90° angulation; group 4 sandblasted with 30µm silica-coated alumina and a 30° angulation; group 5 sandblasted with 82µm zirconia and alumina and a 90° angulation; group 6 sandblasted with 82µm zirconia and alumina and a 30° angulation. Surface roughness (Alicona InfiniteFocus® optical 3-dimensional micro coordinate system), Scanning Electron Microscope (SEM) and Energy Dispersive X-ray Spectroscopy (EDS) analysis were performed in all samples, before and after cleaning procedures with 9,6% hydrofluoric acid and 37% phosphoric acid.

Results: Group 1 had the highest roughness values. Samples sandblasted with 30µm silica-coated alumina and with 82µm alumina and zirconia particles showed higher values of roughness in 30º air abrasion than in 90º procedures, after cleaning protocols. EDS analysis confirmed the presence of silica in zirconia surfaces that were sandblasted with silica-coated alumina particles, even after cleaning protocols. The roughness in all samples presented a decreased after cleaning procedures, indicating the presence of smear-layer, contaminants and dust. Results suggested that the experimental 82µm alumina and zirconia abrasive might produce an appropriate roughness, without leaving a great amount of dust after the air abrasion protocol.

Conclusions: In accordance with the goal of this pilot study, results showed that powder composition, air-abrasion angulation and cleaning procedures are crucial in the quality and quantity of zirconia surface roughness. Despite of this, further studies are needed to fully understand zirconia surface behaviour to roughening procedures, and to perform adhesion tests, once they are the reason of this basic procedure.

1. Introduction

In recent years, a significant effort has been made to improve all-ceramic fixed dental prostheses (FDPs) properties[1–4]. Esthetic demanding, and developments in CAD/CAM technology, with excellent precision milling procedures, have contributed to the growth of all-ceramic unitary, partial and total rehabilitations[5].

Currently, the favorite core material for all-ceramic FDPs is zirconia, a high-strength ceramic, due to its better physical properties when compared to feldspathic, glass and glass-reinforced ceramics[6]. Pure zirconia has a monoclinic crystal structure at room temperature. Zirconia that is used in dentistry mainly contains a tetragonal crystal structure that is partially stabilized with yttrium oxide (YPSZ). External stresses at zirconia surface, such as grinding, cooling, or external impact, may induce a tetragonal to monoclinic phase transformation around and near the tip of the crack, resulting in a 3 to 5% increase of volume. This causes compressive stresses at zirconia surface that counteract with crack propagation – transformation toughening or active crack resistance[7–11]

Usually, zirconia-based frameworks are veneered in order to achieve an improved esthetic appearance. The most frequently used veneering material is the conventional feldspathic ceramic. Despite of that, zirconia can also be veneered with acrylic and composite resins. The latter can be used as a veneer material due to its mechanical properties, in cases where we need a more resilient material, such as in cases where we are dealing with oral parafunctions.

Although there are many clinical studies proving that zirconia is a very stable core material for all-ceramic FDPs, there is a high incidence of fracture or chipping of the veneering material[12–14]. Failure rates due to veneering debonding and fracture are 15% at 2-5 years[15] and according to another study the five year complication rate ranged 10% to 60%[6]. As this is a serious and costly problem in dentistry, practical repair protocols must be developed. Intraoral ceramic repair with resin composite it's an easy and cost-effective clinical procedure, but its clinical success is directly related to the strength levels of resin bonding and adequate surface treatment[16]. Besides, as we move towards to a minimally invasive dentistry, conventional cements need to be left apart as they almost entirely depend on tooth retention, while resin cements depend on high bond strength to zirconia[17,18].

However high bond forces between cements, resin composite and etchable ceramic surfaces can be predictably achieved, conventional acid etching with hydrofluoric acid, has no positive effect on resin bond to zirconia due to its lack of silicon dioxide phase, which is necessary for the creation of microgrooves in zirconia surface[19,20]. Combination of silane coupling agent with Zirconia is also useless as its low percentage of silica prevents the creation of durable siloxane bonding[17]. This problem is being overcome with the development of new zirconia surface treatments. The goal of those surface conditioning procedures is to obtain mechanical and chemical bonding.

Several surface conditioning procedures have been suggested in the literature such as surface grinding[21–24], airborne-particle abrasion using Al_2O_3[18,25–30] selective infiltration etching (SIE)[31–34], silane coupling agents [35–37], tribochemical treatment[38–40], specific primers[41–44], fused glass micro-pearls[1,17,45], surface fluorination [46,47] and laser pretreatment[48–53]. Among these methods there are contradictory results and many of those techniques are unpredictable. Therefore, there's still no consensus or guidelines that lead us to an ideal protocol for bonding to zirconia.

The only imperative step on zirconia bonding procedures in clinical practice seems to be air-abrasion. Despite of the negative effects on flexural strength of zirconia[54,55], airborne-particle abrasion cleans organic contaminants from zirconia surface[56,57] and modifies its energy and wettability[58], increases its microroughness, thus, increasing bonding area and promoting a better mechanical interlocking between composite resin and zirconia and a better long-term bonding[25,59].

After reviewing a large number of publications, it can be noticed that the effect of air abrasion with different inclinations is still not study. Although blasting pressure, particle dimensions and deposition duration have recently been exhaustively examined[29,60], angulation of the sandblasting procedures is still unknown. In all of the studies reviewed, just one used a sandblasting protocol with an inclination different from 90° [61]. There was no study comparing different angulations. This factor might influence the kinetics energy of the sandblasted particles, and potentially produce different roughness patterns that might enhance zirconia surface pre-treatments.

The two main particles used in sandblasting procedures are alumina[25,27–29] and silica-coated modified alumina[38–40]. This pilot study tested an innovative powder for air abrasion procedures, containing 54,5% of Al_2O_3 and 41,5% of ZrO_2 82 µm particles, and a small percentage of TiO_2 and Fe_2O_3 (2,5 and 0,2% respectively). The former abrasives, as they have already been extensively studied, were used as control groups for the new abrasive group. Studying such an experimental abrasive powder and the characterization of its effects on zirconia surface, will improve knowledge about zirconia behavior to air abrasion procedures.

The more variables we can control and understand in air abrasion protocols, the more predictable, successful and less operator sensitive will be this surface pretreatment. Thus, the aim of the present pilot study was to assess the effect of sandblasting angulations, new air abrasion powder containing zirconia, and cleaning procedure on Y-TZP ceramic surface.

2. Materials and methods

2.1. Fabrication of specimens

A total of 4 cylindrical zirconia ceramic disks (ICE Zirkon Translucent, Zirkonzahn, Gais, Italy) of 16 mm diameter and 4 mm height were made in a CAD/CAM machine according to manufacturer's instructions. After sinterization, all disks were polished with rotating silicon carbide paper down to 320 grit (Micro Grinding System Exakt 400 CS, 22851 Norderstedt, Germany) in order to achieve a homogeneous polished surface between all disks.

Customized polyvinyl siloxane mold (Primasil 95, Gerhò, Terlano, Italy) with one cylinder-shaped orifice (2,5 mm in diameter) was placed on the zirconia disks to allow delimitation of the treated area, and divide each disk into three different surface samples.

The disks were divided in 6 different surface treatment groups and for each group 2 samples (n=2) were prepared:

- Group 1: circular areas with machined zirconia (ICE Zirkon Translucent, Zirkonzahn, Gais, Italy), sandblasted with 50 μm alumina powder at 2,5 bar (Airsonic Aluminium-Oxyd Pulver, Hager Werken, Duisburg, Germany) for 15s, at approximately 10 mm away onto the exposed surface, with a 90° angulation, using intraoral air abrasion device (Airsonic Mini Sandblaster, Hager Werken, Duisburg, Germany);
- Group 2: circular areas with machined zirconia (ICE Zirkon Translucent, Zirkonzahn, Gais, Italy), sandblasted with 50 μm alumina powder at 2,5 bar (Airsonic Aluminium-Oxyd Pulver, Hager Werken, Duisburg, Germany) for 15s, at approximately 10 mm away onto the exposed surface, with a 30° angulation, using intraoral air abrasion device (Airsonic Mini Sandblaster, Hager Werken, Duisburg, Germany);
- Group 3: circular areas with machined zirconia (ICE Zirkon Translucent, Zirkonzahn, Gais, Italy), sandblasted with 30 μm silica-coated alumina at 2,5 bar (Cojet™ Sand, 3M ESPE St. Paul, MN, USA) for 15s, at approximately 10 mm away onto the exposed surface, with a 90° angulation, using intraoral air abrasion device (Airsonic Mini Sandblaster, Hager Werken, Duisburg, Germany);
- Group 4: circular areas with machined zirconia (ICE Zirkon Translucent, Zirkonzahn, Gais, Italy), sandblasted with 30 μm silica-coated alumina at 2,5 bar (Cojet™ Sand, 3M ESPE St. Paul, MN, USA) for 15s, at approximately 10 mm away onto the exposed surface, with a 30° angulation, using intraoral air abrasion device (Airsonic Mini Sandblaster, Hager Werken, Duisburg, Germany);
- Group 5: circular areas with machined zirconia (ICE Zirkon Translucent, Zirkonzahn, Gais, Italy), sandblasted with 82 μm zirconia and alumina at 2,5 bar (INDASA, Aveiro, Portugal) for 15s, at

approximately 10 mm away onto the exposed surface, with a 90° angulation, using intraoral air abrasion device (Airsonic Mini Sandblaster, Hager Werken, Duisburg, Germany).

- Group 6: circular areas with machined zirconia (ICE Zirkon Translucent, Zirkonzahn, Gais, Italy), sandblasted with 82 µm zirconia and alumina at 2,5 bar (Indasa, Aveiro, Portugal) for 15s, at approximately 10 mm away onto the exposed surface, with a 30° angulation, using intraoral air abrasion device (Airsonic Mini Sandblaster, Hager Werken, Duisburg, Germany).

All experimental protocol is schematically shown in Figure 1.

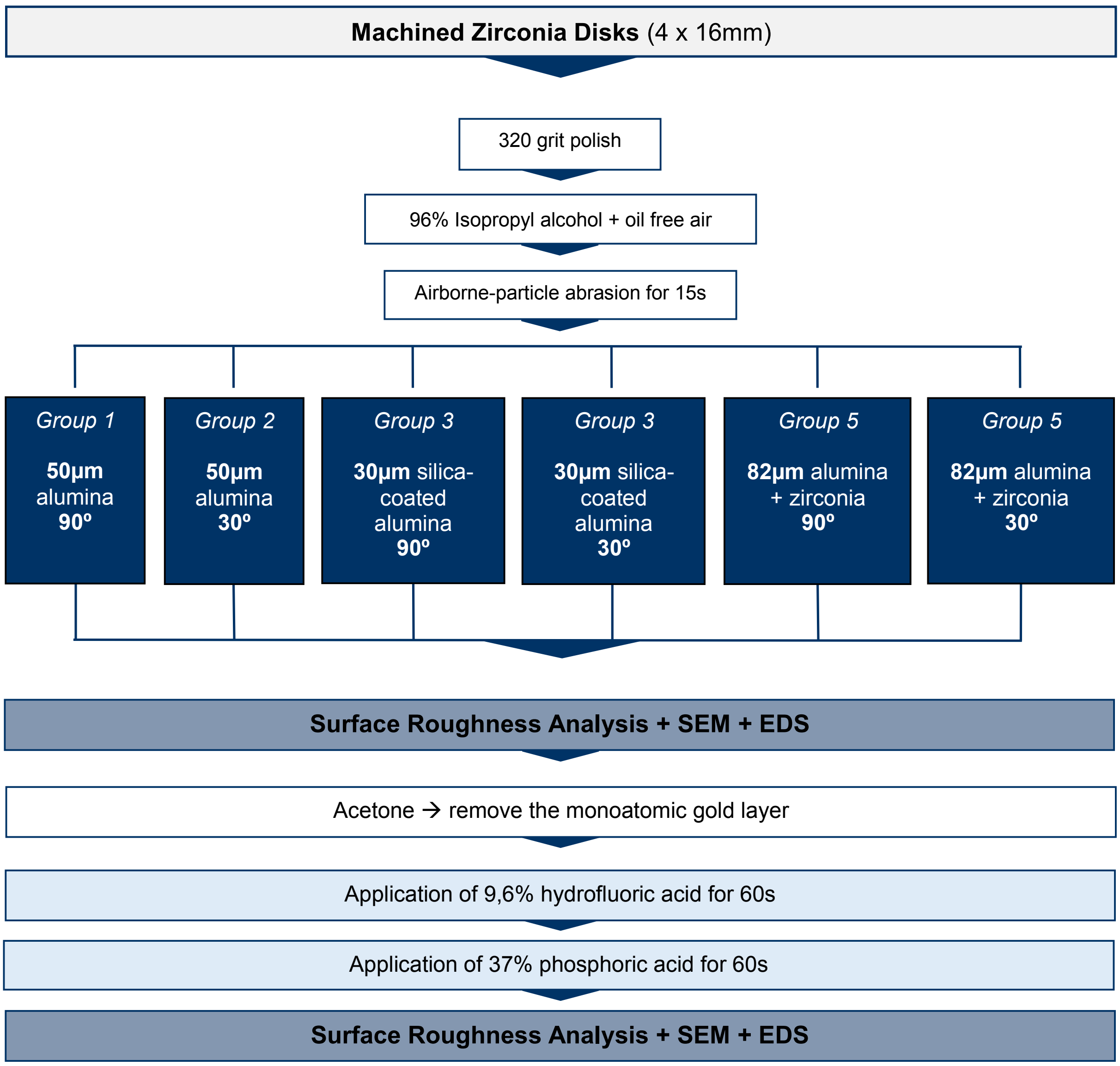

Figure 1. Experimental design of the study.

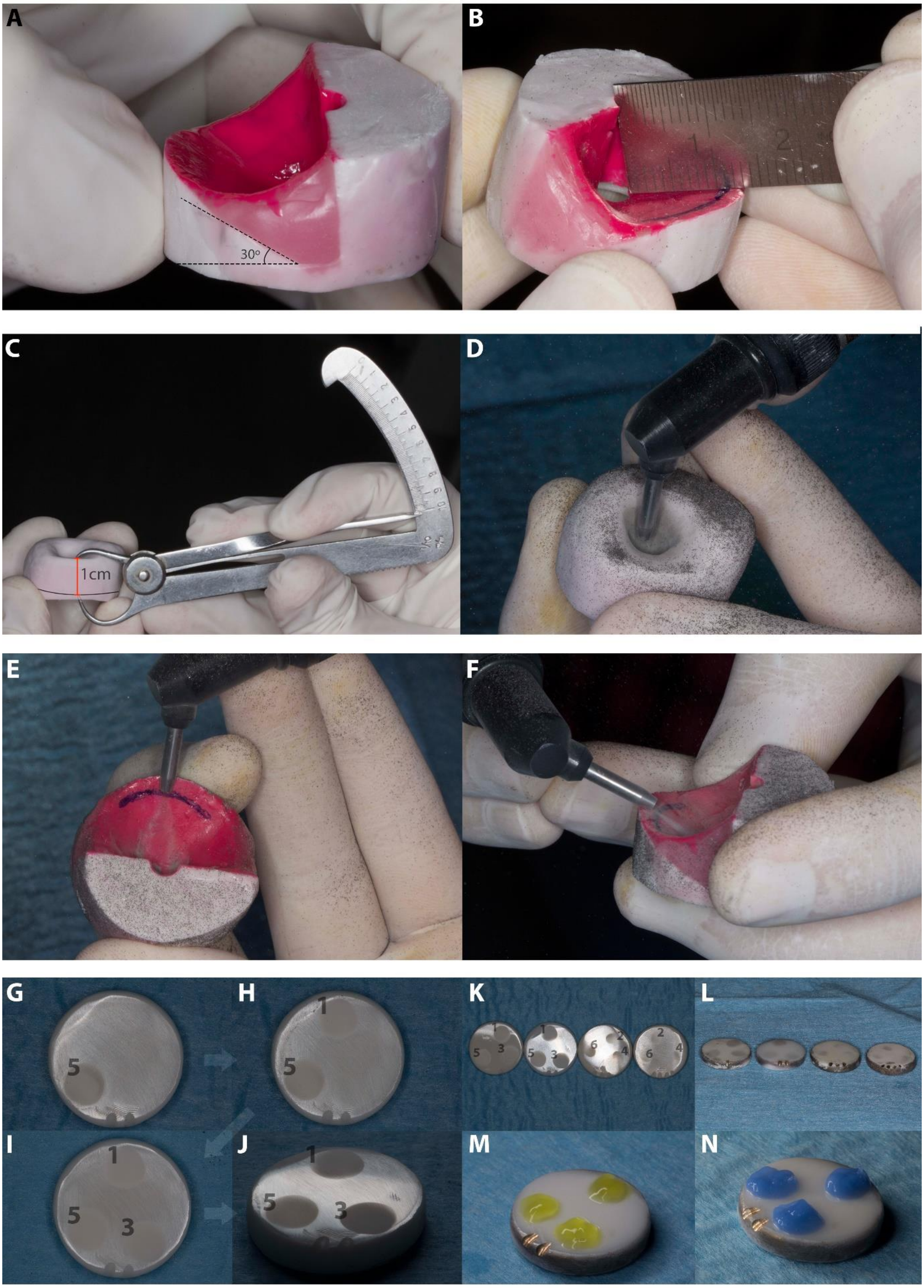

Figure 2. Images of polyvinyl siloxane mold and sample preparation: A and B. Polyvinyl siloxane mold for the 30º air abrasion procedures (groups 2, 4 and 6); C. Polyvinyl siloxane mold for 90º air abrasion procedures (groups 1, 3 and 5); D. 90º sandblasting protocol; E and F. 30º sandblasting protocol; G, H, I and J. Sequence of air abrasion procedures for the same disk; K. All samples after sandblasting protocols, before the first surface analysis; L. All samples after first surface analysis, after acetone cleaning; M. Application of 9,6% hydrofluoric acid; N. Application of 37% phosphoric acid.

2.2. Cleaning of the specimens

In order to allow SEM analysis, a monoatomic gold layer was applied in all samples. Therefore, to prepare the samples for the surface cleaning procedures, acetone was used to remove the latter thin layer. Afterwards, samples were first conditioned with hydrofluoric acid at 9,6 % (Pulpdent Corporation, Watertown, USA) for 60 seconds and then washed and dried with oil-free air. After this, phosphoric acid at 37% (Pulpdent Corporation, Watertown, USA) was applied in order to remove the formed smear layer.

2.3. Surface Roughness

In what concerns surface roughness, its evaluation was made with Alicona InfiniteFocus® (Alicona Imaging GmbH, Grambach/Graz, Austria), which is an optical surface instrument. The latter uses a new technique – focus variation (FV) technology – that evaluates the small depth of focus of an optical system while moving the sensor vertically along the optical axis in order to provide topographical data from the surface. Over-illuminated and under-illuminated surfaces are continuously captured by the optical sensor. Through algorithms, the software converts the obtained data in x, y and z coordinates into 3D information and colour graphics, representing surface roughness. To achieve a random and reliable roughness, avoiding the misleading shape factor, measurements were gathered by tracing an approximately 5mm aleatory path (Figure 3) [62]. The path was made in all the sandblasted areas of the four specimens using a 50x lens.

Alicona IFM version 3.5.1.5 software (Alicona Imaging GmbH,Grambach/Graz, Austria) was used to calculate several parameters to evaluate the surface roughness: **Ra** (average roughness of profile); **Rq** (Root-Mean-Square roughness profile); **Rz** (Mean peak to valley height of roughness profile); **Rc** (Mean height of profile irregularities of roughness profile); **Rsm** (Mean spacing of profile irregularities of roughness profile); **Rsk** (Skewness of roughness profile); and **Rku** (Kurtosis of roughness profile). Regarding skewness measures, Rsk negative values indicate that the surface is made up by valleys, whereas a surface with a positive skewness is said to contain mainly peaks and asperities. Kurtosis measures the sharpness of the profile peaks. A normal curve is given by a value of 3 in a kurtosis parameter. Values lower than 3 represent a surface profile with smoother curves while values

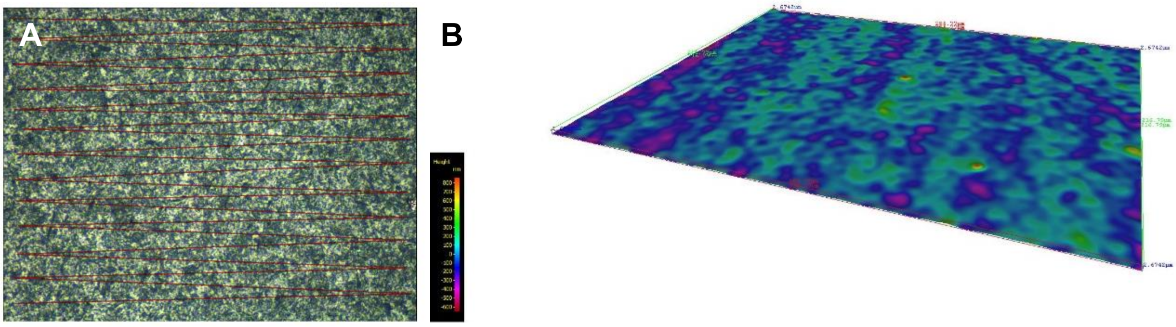

Figure 3. Surface roughness analysis of group 5 sample: A. Random 5mm path; B. Group 5 surface colour graphic

higher than 3 represent a surface profile with sharper curves. Although most of the studies only focus on Ra values to analyze surface roughness, the authors of the present study suggest that a more extensive analysis of the other parameters might be useful in order to attempt to assess the quality of zirconia surface roughness.

2.4. Elemental Composition

Elemental analysis was performed in all sandblasted surfaces using EDS (Energy dispersive X-ray spectroscopy) (Oxford Instruments X-Max, Abingdon, Oxfordshire, United Kingdom) and Aztec Version 1.2 software (Oxford Instruments NanoAnalysis, Abingdon, Oxfordshire, United Kingdom) with a primary electron voltage of 10 kV. The working distance (WD) was set to 20mm.

To control and characterize the used powder, all three abrasive particles were placed in a double sided adhesive conductive carbon taped and their elemental composition were also analyzed.

2.5. Surface Morphology

All samples were used for scanning electron microscope (SEM) analysis, before and after cleaning procedures. After vacuum sputtering with gold, the samples were analyzed under x2000, x10000 and x20000 magnification (JEOL JSM – 5310 Scanning Microscope, Tokyo, Japan). The acceleration voltage of the cathode was set to 10 kV. The three abrasive particles were also subjected to SEM analysis under 350x magnification.

3. Results

Tables I-XIV present the obtained roughness values before and after acidic cleaning procedures. Green values are the higher ones. Once Rsm parameter must be analyzed at the same time with other parameters to assess if higher or lower values are necessary for a particularly situation, it wasn't accounted in the tables below.

Table I. Roughness analysis values for each sample, before cleaning procedures.

	Ra (nm)	Rq (nm)	Rz (nm)	Rc (nm)	Rsm (nm)	Rsk	Rku
1	235,98	296,94	1373,00	825,29	94260,00	-0,796	2,953
	146,73	187,24	1068,20	573,52	48656,00	-0,349	3,239
2	124,43	163,34	990,69	569,33	103050,00	-0,788	4,225
	82,65	105,81	700,95	348,36	48159,00	-0,412	3,834
3	104,46	133,18	710,80	417,19	58485,00	-0,575	3,403
	78,62	101,90	619,23	373,96	67733,00	-0,634	6,838
4	127,84	167,22	900,60	502,04	69219,00	-1,051	4,203
	133,29	163,91	826,20	453,99	61574,00	-0,386	2,800
5	110,45	138,95	900,23	478,64	48738,00	-0,032	3,391
	83,61	105,29	677,58	342,61	46580,00	-0,128	3,308
6	109,11	138,71	900,47	475,91	65405,00	0,222	3,780
	75,71	97,79	718,14	358,97	53177,00	0,270	4,305

Table II. Mean values of the roughness parameters in the 6 groups, before cleaning procedures.

	Ra (nm)	Rq (nm)	Rz (nm)	Rc (nm)	Rsm (nm)	Rsk	Rku
1	191,36	242,09	1220,60	699,41	71458,00	-0,572	3,096
2	103,54	134,58	845,82	458,85	75604,50	-0,600	4,030
3	91,54	117,54	665,02	395,58	63109,00	-0,605	5,120
4	130,57	165,57	863,40	478,02	65396,50	-0,719	3,501
5	97,03	122,12	788,91	410,63	47659,00	-0,080	3,350
6	92,41	118,25	809,31	417,44	59291,00	0,246	4,042

Table III. Mean values of the roughness parameters in groups with the same angulations, before cleaning procedures.

90°	Ra (nm)	Rq (nm)	Rz (nm)	Rc (nm)	Rsm (nm)	Rsk	Rku
1	191,36	242,09	1220,60	699,41	71458,00	-0,572	3,096
3	91,54	117,54	665,02	395,58	63109,00	-0,605	5,120
5	97,03	122,12	788,91	410,63	47659,00	-0,080	3,350

30°	Ra (nm)	Rq (nm)	Rz (nm)	Rc (nm)	Rsm (nm)	Rsk	Rku
2	103,54	134,58	845,82	458,85	75604,50	-0,600	4,030
4	130,57	165,57	863,40	478,02	65396,50	-0,719	3,501
6	92,41	118,25	809,31	417,44	59291,00	0,246	4,042

Table IV. Mean values of the roughness parameters in groups with the same abrasive particles, before cleaning procedures.

	Ra (nm)	Rq (nm)	Rz (nm)	Rc (nm)	Rsm (nm)	Rsk	Rku
1, 2	147,45	188,33	1033,21	579,13	73531,25	-0,586	3,563
3, 4	111,05	141,55	764,21	436,80	64252,75	-0,662	4,311
5, 6	94,72	120,19	799,11	414,03	53475,00	0,083	3,696

Table V. Mean values of the roughness parameters between the two different sandblasting angulations, before cleaning procedures.

	Ra (nm)	Rq (nm)	Rz (nm)	Rc (nm)	Rsm (nm)	Rsk	Rku
90°	126,64	160,58	891,51	501,87	60742,00	-0,419	3,855
30°	108,84	139,46	839,51	451,43	66764,00	-0,358	3,858

Table VI. Roughness analysis values for each sample, after cleaning procedures.

	Ra (nm)	Rq (nm)	Rz (nm)	Rc (nm)	Rsm (nm)	Rsk	Rku
1	142,34	177,46	973,32	544,43	56185,00	-0,233	2,919
	90,18	114,81	724,43	360,50	43040,00	-0,592	3,654
2	82,08	103,47	612,24	308,23	55595,00	-0,224	3,214
	60,07	77,37	522,88	261,18	54645,00	-0,263	3,708
3	107,79	135,10	825,20	436,29	49239,00	-0,235	3,222
	65,95	83,76	472,48	255,40	45065,00	-0,367	3,165
4	64,92	80,42	447,87	241,75	38457,00	-0,094	2,837
	116,77	144,71	755,79	456,94	111700,00	-0,422	3,018
5	89,66	115,38	690,22	375,89	47884,00	-0,412	3,742
	88,35	110,39	688,72	365,13	55149,00	-0,233	3,276
6	103,85	140,51	897,33	501,87	102390,00	-0,469	5,041
	77,96	101,30	590,72	324,66	60397,00	-0,393	3,541

Table VII. Mean values of the roughness parameters in the 6 groups, after cleaning procedures.

	Ra (nm)	Rq (nm)	Rz (nm)	Rc (nm)	Rsm (nm)	Rsk	Rku
1	116,26	146,14	848,88	452,47	49612,50	-0,413	3,287
2	71,08	90,42	567,56	284,71	55120,00	-0,243	3,461
3	86,87	109,43	648,84	345,85	47152,00	-0,301	3,193
4	90,84	112,57	601,83	349,35	75078,50	-0,258	2,928
5	89,00	112,89	689,47	370,51	51516,50	-0,323	3,509
6	90,90	120,91	744,03	413,27	81393,50	-0,431	4,291

Table VIII. Mean values of the roughness parameters in groups with the same angulations, after cleaning procedures.

90°	Ra (nm)	Rq (nm)	Rz (nm)	Rc (nm)	Rsm (nm)	Rsk	Rku
1	116,26	146,14	848,88	452,47	49612,50	-0,413	3,287
3	86,87	109,43	648,84	345,85	47152,00	-0,301	3,193
5	89,00	112,89	689,47	370,51	51516,50	-0,323	3,509

30°	Ra (nm)	Rq (nm)	Rz (nm)	Rc (nm)	Rsm (nm)	Rsk	Rku
2	71,08	90,42	567,56	284,71	55120,00	-0,243	3,461
4	90,84	112,57	601,83	349,35	75078,50	-0,258	2,928
6	90,90	120,91	744,03	413,27	81393,50	-0,431	4,291

Table IX. Mean values of the roughness parameters in groups with the same abrasive particles, after cleaning procedures.

	Ra (nm)	Rq (nm)	Rz (nm)	Rc (nm)	Rsm (nm)	Rsk	Rku
1, 2	93,67	118,28	708,22	368,59	52366,25	-0,328	3,374
3, 4	88,86	111,00	625,34	347,60	61115,25	-0,279	3,061
5, 6	89,95	116,90	716,75	391,89	66455,00	-0,377	3,900

Table X. Mean values of the roughness parameters between the two different sandblasting angulations, after cleaning procedures.

	Ra (nm)	Rq (nm)	Rz (nm)	Rc (nm)	Rsm (nm)	Rsk	Rku
90°	97,38	122,82	729,06	389,61	49427,00	-0,345	3,330
30°	84,27	107,96	637,81	349,11	70530,67	-0,311	3,560

Table XI. Comparison of the mean roughness values between the same groups, before and after cleaning procedures.

	Ra (nm)	Rq (nm)	Rz (nm)	Rc (nm)	Rsm (nm)	Rsk	Rku
1 Before	191,36	242,09	1220,60	699,41	71458,00	-0,572	3,096
1 After	116,26	146,14	848,88	452,47	49612,50	-0,413	3,287
2 Before	103,54	134,58	845,82	458,85	75604,50	-0,600	4,030
2 After	71,08	90,42	567,56	284,71	55120,00	-0,243	3,461
3 Before	91,54	117,54	665,02	395,58	63109,00	-0,605	5,120
3 After	86,87	109,43	648,84	345,85	47152,00	-0,301	3,193
4 Before	130,57	165,57	863,40	478,02	65396,50	-0,719	3,501
4 After	90,84	112,57	601,83	349,35	75078,50	-0,258	2,928
5 Before	97,03	122,12	788,91	410,63	47659,00	-0,080	3,350
5 After	89,00	112,89	689,47	370,51	51516,50	-0,323	3,509
6 Before	92,41	118,25	809,31	417,44	59291,00	0,246	4,042
6 After	90,90	120,91	744,03	413,27	81393,50	-0,431	4,291

Table XII. Comparison of the mean roughness values between groups with the same abrasive particles, before and after cleaning procedures

	Ra (nm)	Rq (nm)	Rz (nm)	Rc (nm)	Rsm (nm)	Rsk	Rku
1, 2 Before	147,45	188,33	1033,21	579,13	73531,25	-0,586	3,563
1, 2 After	93,67	118,28	708,22	368,59	52366,25	-0,328	3,374
3, 4 Before	111,05	141,55	764,21	436,80	64252,75	-0,662	4,311
3, 4 After	88,86	111,00	625,34	347,60	61115,25	-0,279	3,061
5, 6 Before	94,72	120,19	799,11	414,03	53475,00	0,083	3,696
5, 6 After	89,95	116,90	716,75	391,89	66455,00	-0,377	3,900

Table XIII. Comparison of the mean roughness values between the two different sandblasting angulations, before and after cleaning procedures

	Ra (nm)	Rq (nm)	Rz (nm)	Rc (nm)	Rsm (nm)	Rsk	Rku
90° Before	126,64	160,58	891,51	501,87	60742,00	-0,419	3,855
90° After	97,38	122,82	729,06	389,61	49427,00	-0,345	3,330
30° Before	108,84	139,46	839,51	451,43	66764,00	-0,358	3,858
30° After	84,27	107,96	637,81	349,11	70530,67	-0,311	3,560

Table XIV. Highest roughness values summary table, comparing before and after cleaning procedures measurements

	Roughness	Ra	Rq	Rz	Rc	Rsk	Rku
Before	1 vs 2 vs 3 vs 4 vs 5 vs 6	1	1	1	1	4	1
	(90°) 1 vs 3 vs 5	1	1	1	1	3	1
	(30°) 2 vs 4 vs 6	4	4	4	4	4	4
	(Al) 1, 2 vs (Si) 3, 4 vs (Zr) 5, 6	Al	Al	Al	Al	Si	Si
	90° vs 30°	90°	90°	90°	90°	90°	90°
After	1 vs 2 vs 3 vs 4 vs 5 vs 6	1	1	1	1	6	4
	(90°) 1 vs 3 vs 5	1	1	1	1	1	3
	(30°) 2 vs 4 vs 6	6	6	6	6	6	4
	(Al) 1, 2 vs (Si) 3, 4 vs (Zr) 5, 6	Al	Al	Zr	Zr	Zr	Si
	90° vs 30°	90°	90°	90°	90°	90°	90°
Before vs After	1 vs 1	Before	Before	Before	Before	Before	Before
	2 vs 2	Before	Before	Before	Before	Before	After
	3 vs 3	Before	Before	Before	Before	Before	After
	4 vs 4	Before	Before	Before	Before	Before	After
	5 vs 5	Before	Before	Before	Before	After	Before
	6 vs 6	Before	Before	Before	Before	After	Before
	Al vs Al	Before	Before	Before	Before	Before	After
	Si vs Si	Before	Before	Before	Before	Before	After
	Zr vs Zr	Before	Before	Before	Before	After	Before
	90° vs 90°	Before	Before	Before	Before	Before	After
	30° vs 30°	Before	Before	Before	Before	Before	After

Tables XV-XXIV present the obtained EDS analysis values before and after acidic cleaning procedures. Green values are the higher ones and red values suggest contamination of the samples.

Table XV. EDS analysis of the Zr, Al and Si elements for each sample, before cleaning procedures.

	Zr (%)	Al (%)	Si (%)
1	30,7	3,2	0,0
	30,8	2,9	0,0
2	29,9	0,9	1,0
	32,7	2,1	0,0
3	29,3	1,7	3,3
	29,0	1,8	3,0
4	28,6	1,3	2,3
	31,3	0,9	1,5
5	30,3	2,6	0,0
	31,6	3,3	0,0
6	30,4	1,8	0,0
	35,2	0,7	0,0

Table XVI. Mean percentage values of Zr, Al and Si elements of EDS analysis in the 6 groups, before cleaning procedures.

	Zr (%)	Al (%)	Si (%)
1	30,75	3,05	0,00
2	31,30	1,50	0,50
3	29,15	1,75	3,15
4	29,95	1,10	1,90
5	30,95	2,95	0,00
6	32,80	1,25	0,00

Table XVII. Mean percentage values of Zr, Al and Si elements of EDS analysis in groups with the same abrasive particles, before cleaning procedures.

	Zr (%)	Al (%)	Si (%)
1, 2	31,03	2,28	0,25
3, 4	29,55	1,43	2,53
5, 6	31,88	2,10	0,00

Table XVIII. Mean percentage values of Zr, Al and Si elements of EDS analysis between the two different sandblasting angulations, before cleaning procedures.

	Zr (%)	Al (%)	Si (%)
90°	30,28	2,58	1,05
30°	31,35	1,28	0,80

Table XIX. EDS analysis of the Zr, Al and Si elements for each sample, after cleaning procedures.

	Zr (%)	Al (%)	Si (%)
1	26,0	1,8	1,3
	29,4	1,7	1,0
2	34,1	0,6	1,1
	35,4	1,4	0,0
3	54,2	0,9	0,0
	34,2	1,2	0,8
4	34,3	0,6	1,0
	35,4	0,6	0,9
5	35,0	2,3	0,0
	35,0	2,1	1,5
6	30,8	1,7	0,0
	37,2	0,9	0,8

Table XX. Mean percentage values of Zr, Al and Si elements of EDS analysis in the 6 groups, after cleaning procedures.

	Zr (%)	Al (%)	Si (%)
1	27,70	1,75	1,15
2	34,75	1,00	0,55
3	44,20	1,05	0,40
4	34,85	0,60	0,95
5	35,00	2,20	0,75
6	34,00	1,30	0,40

Table XXI. Mean percentage values of Zr, Al and Si elements of EDS analysis in groups with the same abrasive particles, after cleaning procedures.

	Zr (%)	Al (%)	Si (%)
1, 2	31,23	1,38	0,85
3, 4	39,53	0,83	0,68
5, 6	34,50	1,75	0,58

Table XXII. Mean percentage values of Zr, Al and Si elements of EDS analysis between the two different sandblasting angulations, after cleaning procedures.

	Zr (%)	Al (%)	Si (%)
90°	35,63	1,67	0,77
30°	34,53	0,97	0,63

Table XXIII. Comparison of EDS analysis values between groups with the same abrasive particles, before and after cleaning procedures

	Zr (%)	Al (%)	Si (%)
1, 2 Before	31,03	2,28	0,25
1, 2 After	31,23	1,38	0,85
3, 4 Before	29,55	1,43	2,53
3, 4 After	39,53	0,83	0,68
5, 6 Before	31,88	2,10	0,00
5, 6 After	34,50	1,75	0,58

Table XXIV. Comparison of EDS analysis values between the two different sandblasting angulations, before and after cleaning procedures

	Zr (%)	Al (%)	Si (%)
90° Before	30,28	2,58	1,05
90° After	35,63	1,67	0,77
30° Before	31,35	1,28	0,80
30° After	34,53	0,97	0,63

Table XXIV. Highest EDS analysis values summary table, comparing before and after cleaning procedures measurements

	EDS	Zr	Al	Si
Before	1 vs 2 vs 3 vs 4 vs 5 vs 6	6	1	3
	(Al) 1, 2 vs (Si) 3, 4 vs (Zr) 5, 6	Zr	Al	Si
	90° vs 30°	30°	90°	90°
After	1 vs 2 vs 3 vs 4 vs 5 vs 6	3	5	1 (contamination)
	(Al) 1, 2 vs (Si) 3, 4 vs (Zr) 5, 7	Si	Zr	Al (contamination)
	90° vs 30°	90°	90°	90°
Before vs After	Al vs Al	After	Before	After (contamination)
	Si vs Si	After	Before	Before
	Zr vs Zr	After	Before	After (contamination)
	90° vs 90°	After	Before	Before
	30° vs 30°	After	Before	Before

Group 1 presented the highest roughness results for the Ra, Rq, Rz, Rc and Rku parameters before cleaning procedures. Group 4 presented the surface with higher values of valleys. From all the groups sandblasted with an angulation of 90º, group 1 presented all the highest values of roughness, except for the Rsk value, which was higher in group 3. Group 4 had all the highest values of roughness when comparing groups with 30º sandblasting protocols. 50µm alumina sandblasting resulted in higher values of Ra, Rq, Rz and Rc when compared to the other abrasives. Tribochemical silica-coating treatment resulted in a surface with softer irregularities (Rku) and high values of valleys (Rsk). 90º sandblasting created a rougher surface than the 30º method.

In accordance to what happen before cleaning procedures, group 1 presented the highest values of roughness for the Ra, Rq, Rz and Rc parameters after cleaning with hydrofluoric acid and phosphoric acid. For the other hand, after cleaning, group 6 presented the highest level of valleys and group 4 obtained smoother and less sharp peaks patterns. . From all the groups sandblasted with an angulation of 90º, group 1 presented all the highest values of roughness, except for the Rku value, which was higher in group 3. Group 6 had all the highest values of roughness when comparing groups with 30º sandblasting protocols, except for Rku value which, again, was the highest for group 4. Alumina airborne particle abrasion presented the highest levels of Ra and Rq parameters, while the new experimental sandblasting powder presented the highest values in Rz, Rc and Rsk parameters. Cojet™ sand had the best Rku values. Just like before cleaning procedures, 90º air abrasion resulted in higher surface roughness parameters.

After cleaning procedures, all parameters of roughness decreased for abrasion with 50 µm particles and Cojet™ sand, other than Rku values. Groups 5 and 6 presented lower roughness measurements for all parameters, except for the Rsk, that had better values after cleaning methods.

90º and 30º sandblasting protocols had higher levels of roughness before cleaning procedures, other than Rku parameter

Group 1 presented higher values of roughness for all parameters before cleaning procedures. Group 2, 3 and 4 had higher values of roughness in all parameters before cleaning procedures, except for the Rku parameter. Group 5 and 6 had higher measurements of roughness for all parameters before cleaning with hydrofluoric and phosphoric acids, except for the Rsk parameter.

In what concerns EDS analysis before acidic cleaning methods, group 1 presented the highest percentage of Al element, group 3 the highest percentage of Si element, and group 6 the highest value of Zr element. As expected, 50 µm alumina sandblasting resulted in a surface with the highest mean percentage of Al element, Cojet™ presented the highest value of Si element surface content and 82 µm mixture of zirconia and alumina created a surface with the highest mean percentage of zirconia. Before cleaning, Zirconia surface had higher percentage of Al and Si elements when it was sandblasted with a perpendicular angulation, while Zr element had the highest percentage on zirconia surface using 30º air abrasion.

EDS analysis after cleaning protocols revealed higher mean percentage values of Zr element in the group 3. Group 5 had the highest value of Al element while group 1 had the highest percentage of Si element. Silica-coated alumina abrasive had higher mean percentage of Zr element on zirconia surface. Groups 5 and 6 had the highest values of Al element and groups 1 and 2 had the highest mean percentage of Si element. When sandblasting with a 90º angulation, higher values of Zr, Al and Si elements are measured in the treated zirconia surface.

Groups 1, 2, 5 and 6 had higher Zr and Si elements after cleaning procedures, while Al element was higher before cleaning protocols. Surfaces treated with Cojet™ sand had higher values of Al and Si element before cleaning procedures, while higher values of Zr were achieved after cleaning protocols.

90º and 30º sandblasting protocols created higher values of Zr element after cleaning, while the highest values of Al and Si elements were achieved before cleaning methods.

SEM analysis of the 6 different groups after cleaning procedures with hydrofluoric and phosphoric acids, revealed heterogeneous treated areas, and a common random tracing made by the acid container tip on zirconia treated surface (Figure 4).

Morphological analysis (SEM) of each air abrasion powder showed that abrasive with 82µm zirconia and alumina particles and the abrasive with 50µm alumina particles have heterogeneous and sharp particles, while Cojet™ sand has a mixture of sharp and spherical abrasive particles. The latter particles seem to have much more silica content when compared to the sharper ones. The spherical Cojet™ particles have a semi-quantitative 5,2% of Si element and 0,4% of Al element, while the sharper particles have a semi-quantitative 9,6% of Al element and 1,3% of Si element (figure 5).

Before cleaning procedures, SEM Images from groups sandblasted with silica-coated alumina seem to have much more dust and loose particles when compared to areas treated with the other abrasive particles (Figures 6 and 7). After cleaning methods, all treated areas seem to be more spongy and porous when compared to the same areas before cleaning procedures (Figures 9, 10, 11 and 13).

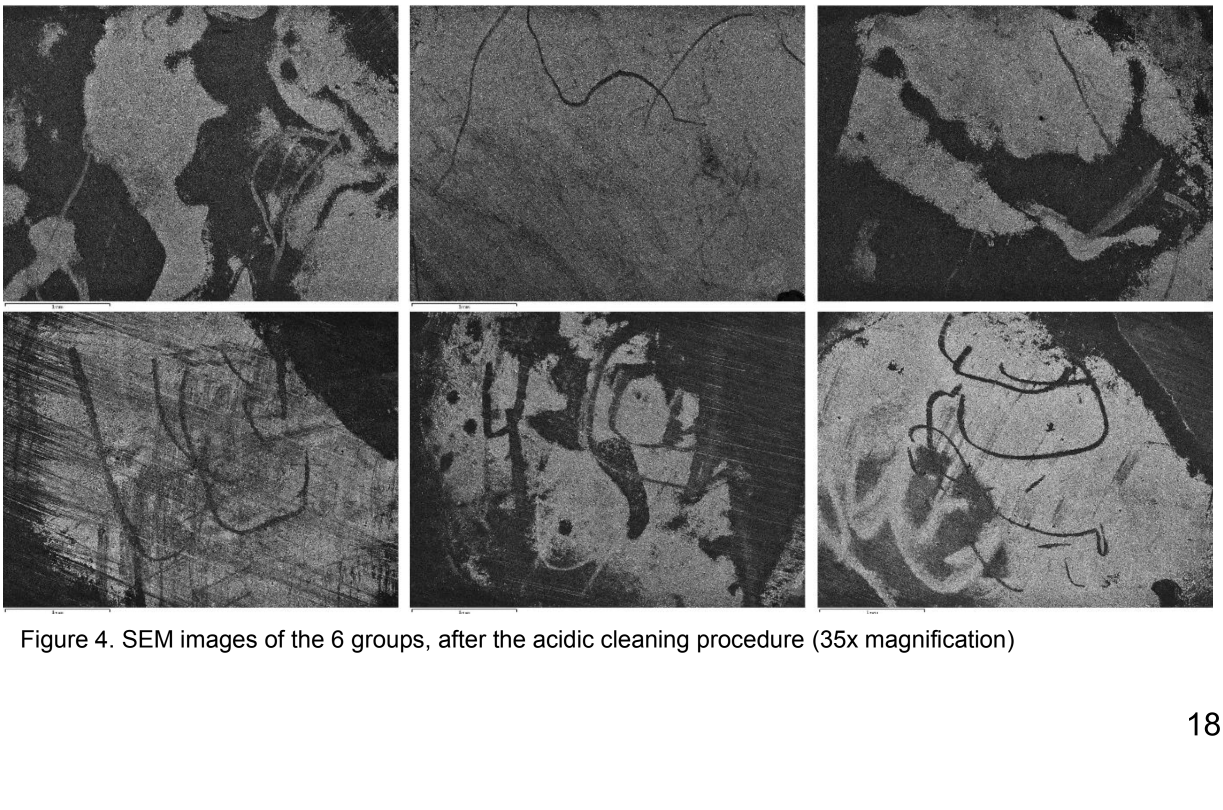

Figure 4. SEM images of the 6 groups, after the acidic cleaning procedure (35x magnification)

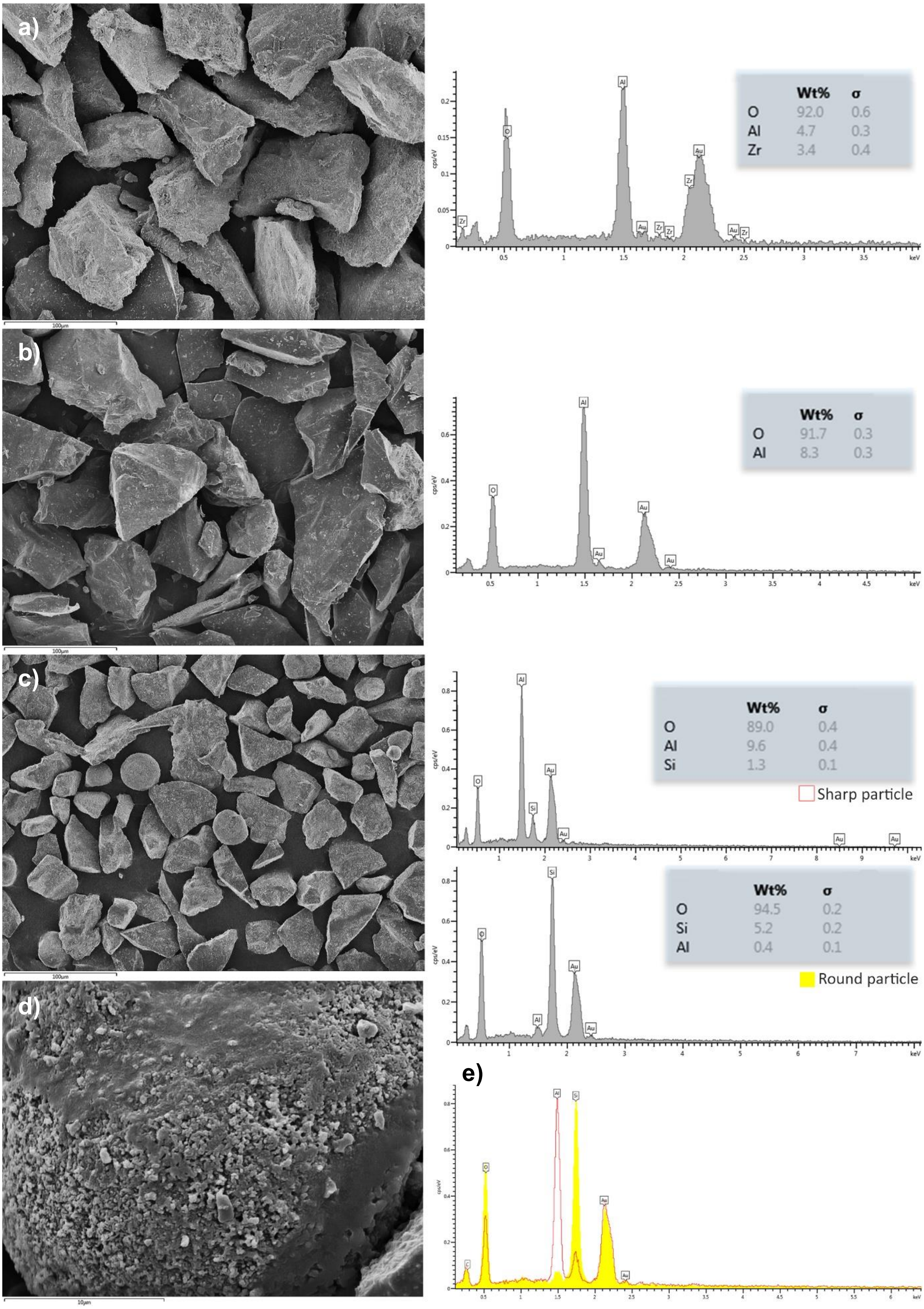

Figure 5. SEM and EDS abrasive analysis: a) 82μm zirconia and alumina particles (350x); b) 50μm alumina particles(350x); c) 30μm silica-coated alumina particle (350x); d) Nano-silica-coated alumina particles from Cojet™ sand surface (5000x); e) Comparison of EDS analysis of a round and a sharp particles of Cojet™ sand

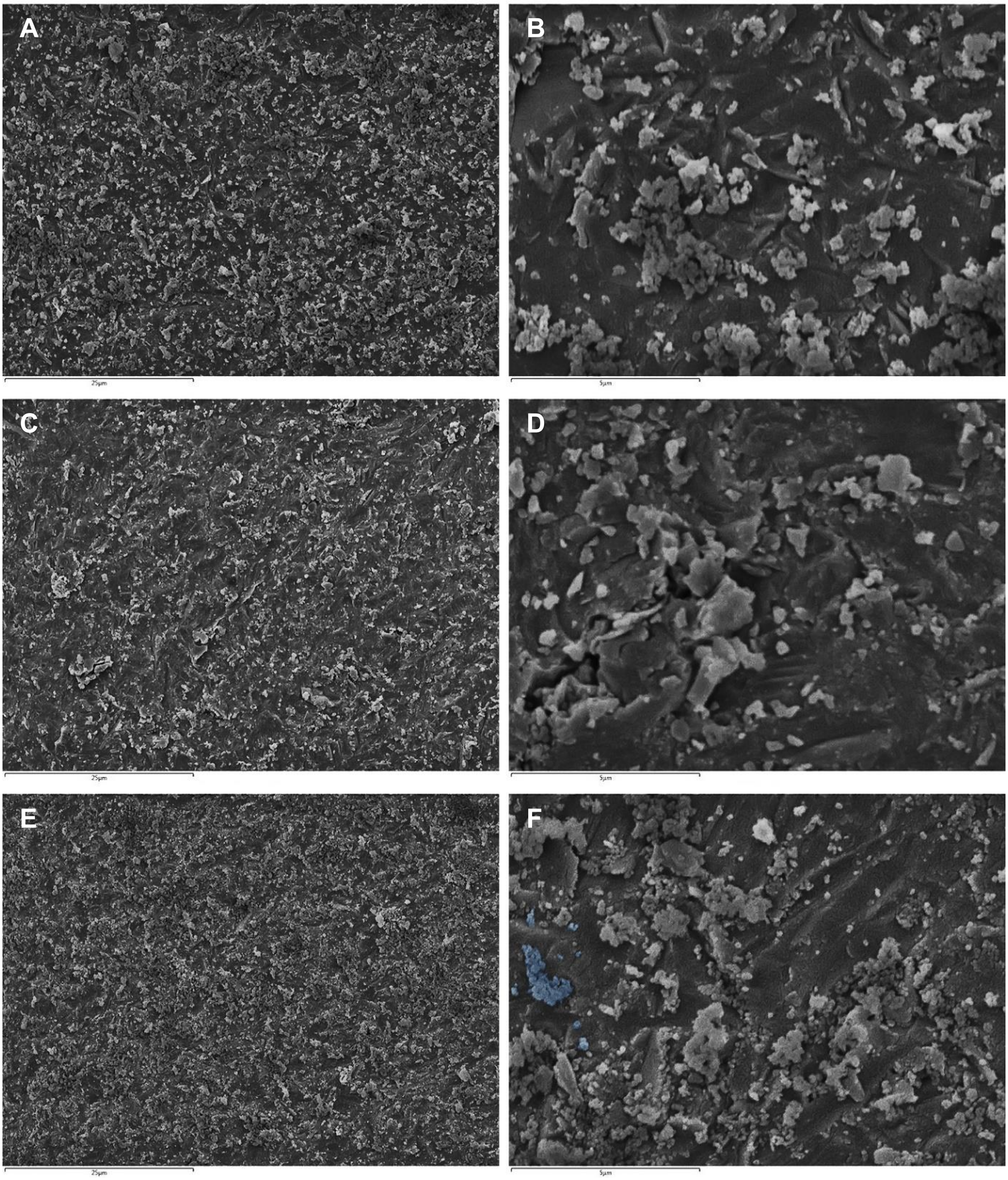

Figure 6. SEM images from groups sandblasted at 30º, before cleaning procedures: A and B. Group 2, 2000x and 10000x magnification, respectively; C and D. Group 6, 2000x and 10000x magnification, respectively; E and F. Group 4, 2000x and 10000x, respectively (blue highlights represent nano-silica particles).

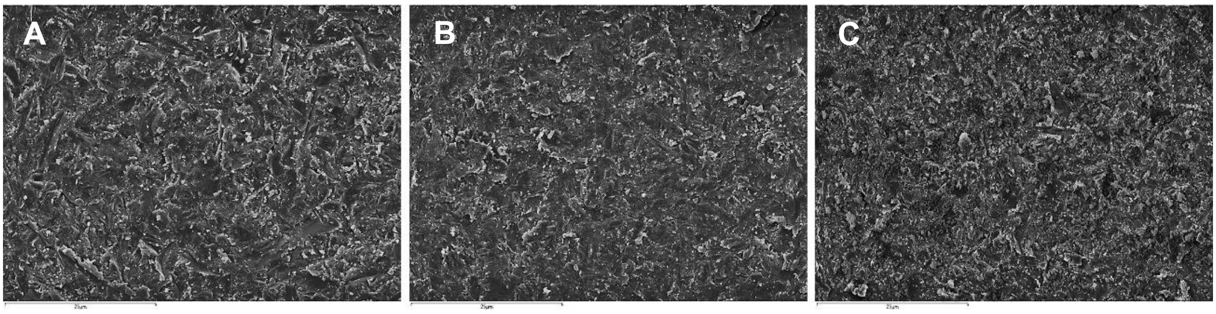

Figure 7. SEM images from groups sandblasted at 90º, before cleaning procedures (2000x magnification): A Group 1; B. Group 5; C. Group 3

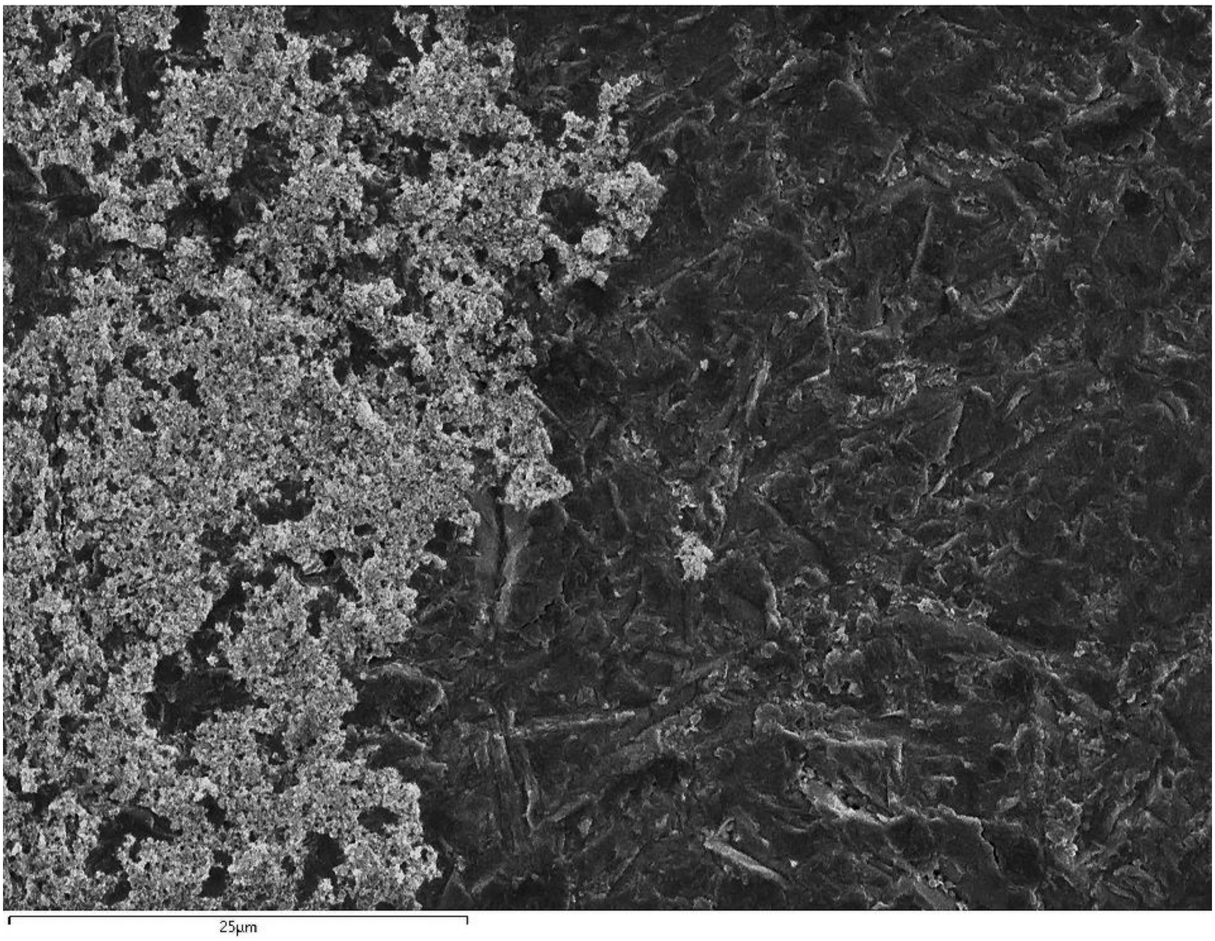

Figure 8. SEM image from a transition zone between group 1 treated area (left) and untreated (right) zirconia surface, after cleaning procedures.

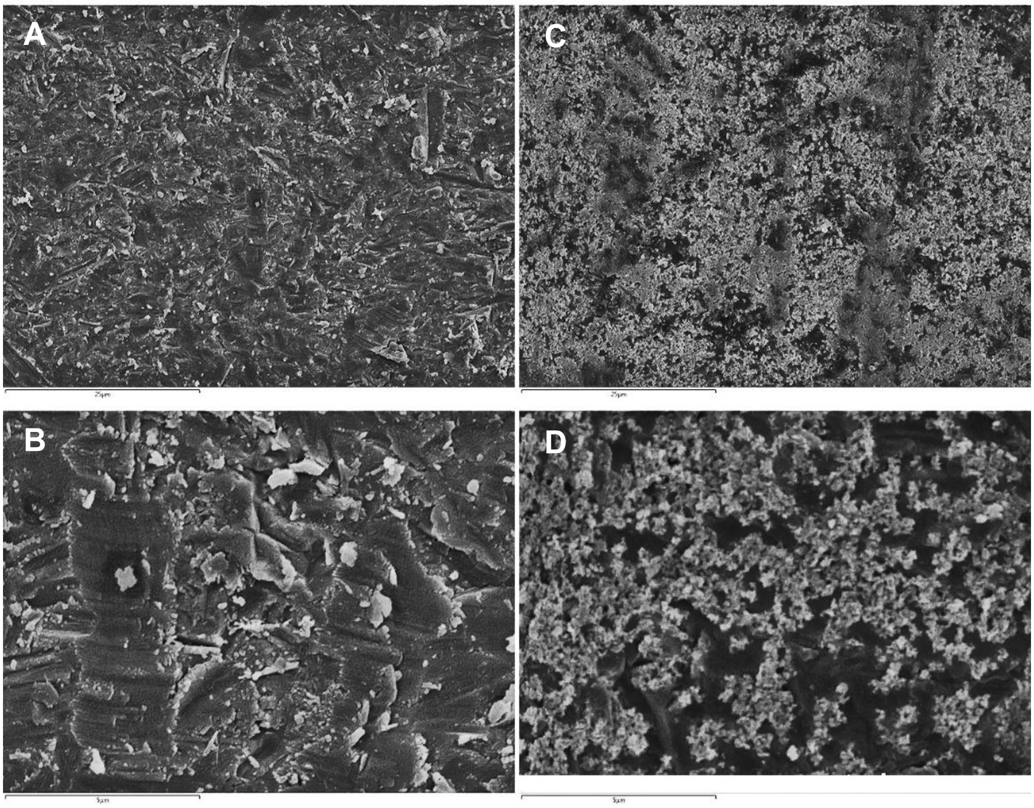

Figure 9. SEM images from group 2: A and B. Before cleaning procedures (2000x and 10000x, respectively); C and D. After cleaning procedures (2000x and 10000x, respectively)

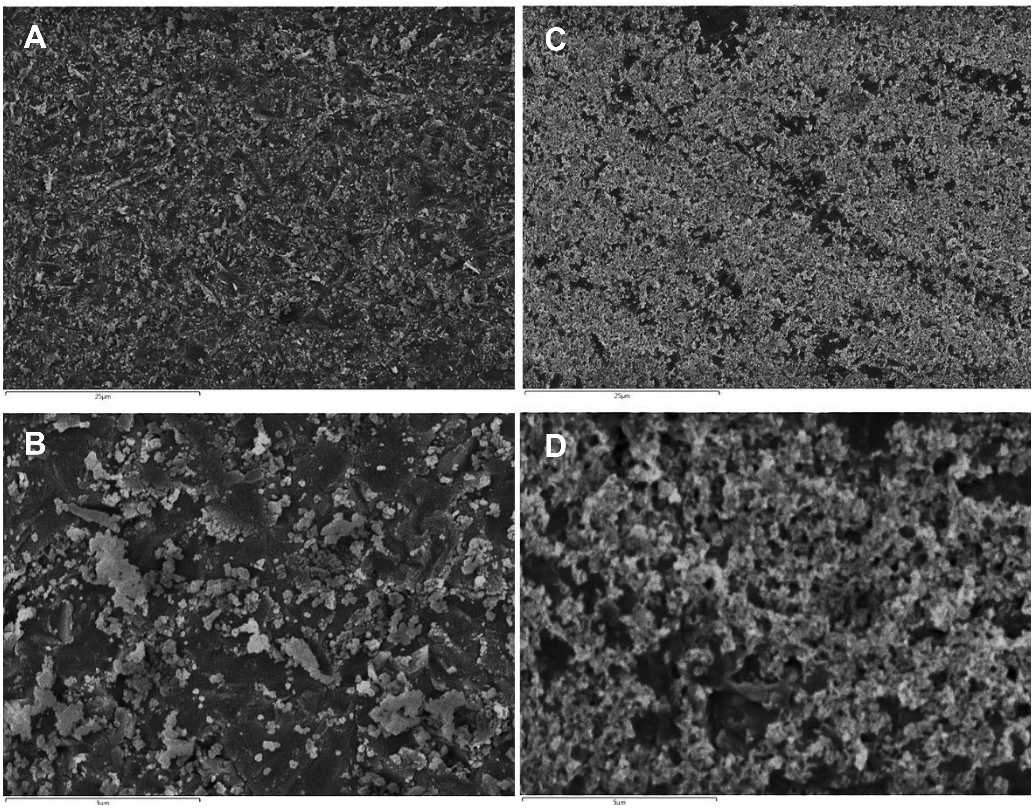

Figure 10. SEM images from group 4: A and B. Before cleaning procedures (2000x and 10000x, respectively); C and D. After cleaning procedures (2000x and 10000x, respectively)

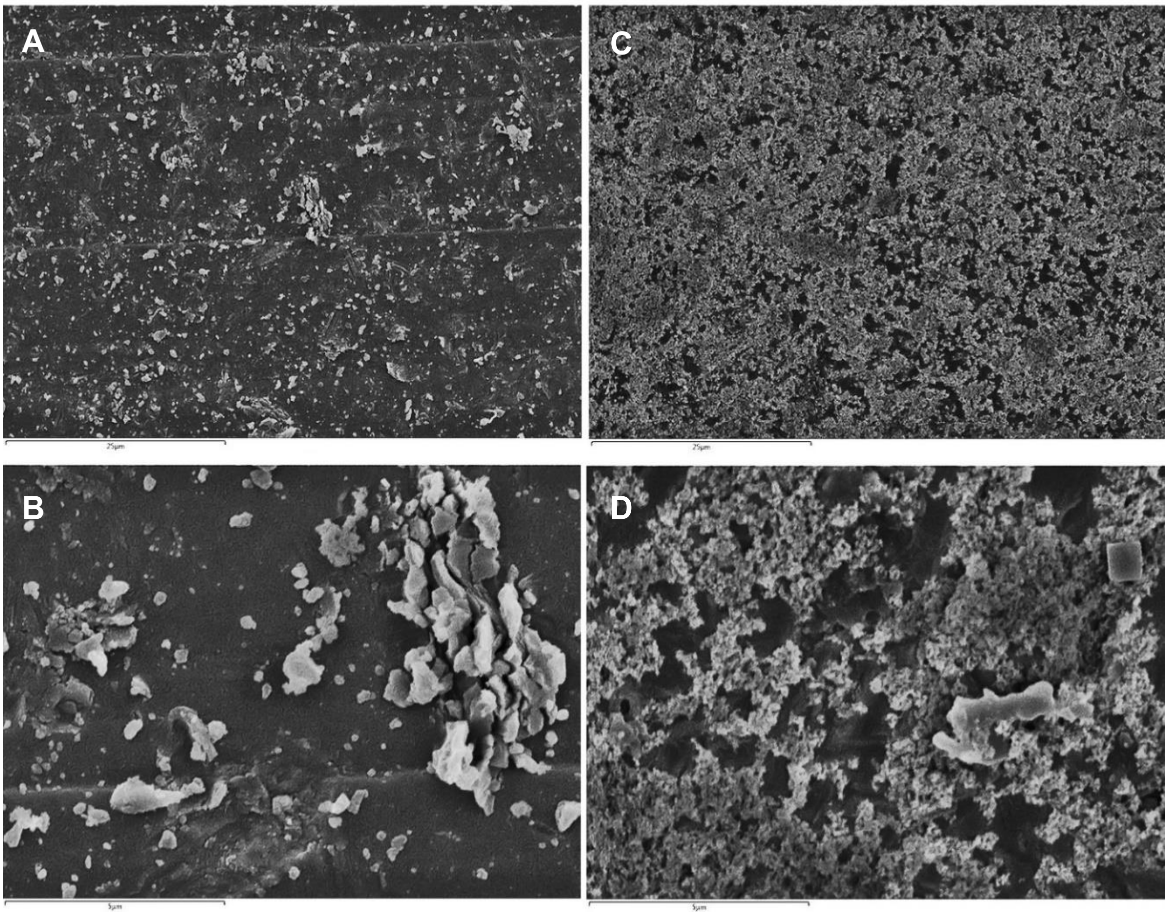

Figure 11. SEM images from group 6: A and B. Before cleaning procedures (2000x and 10000x, respectively); C and D. After cleaning procedures (2000x and 10000x, respectively)

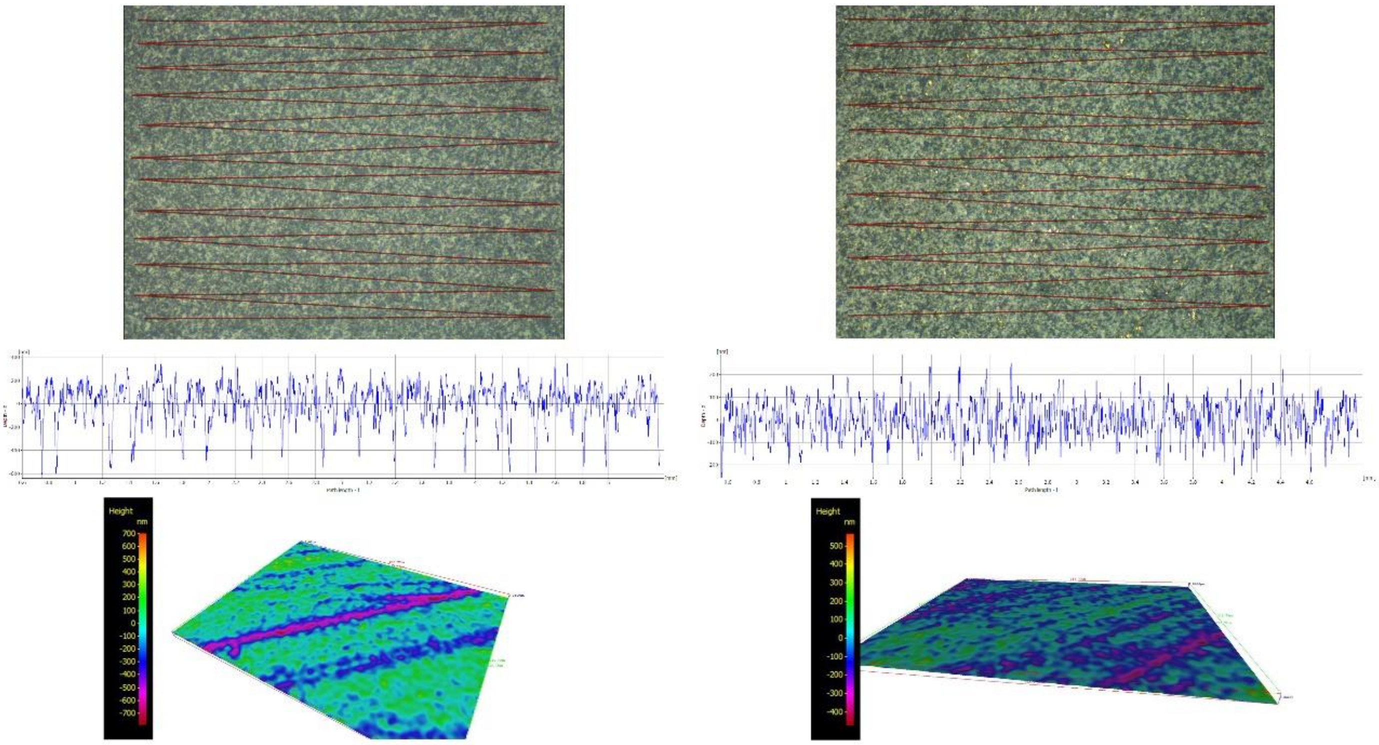

Figure 12. Comparison between group 3 before and after cleaning procedures results.

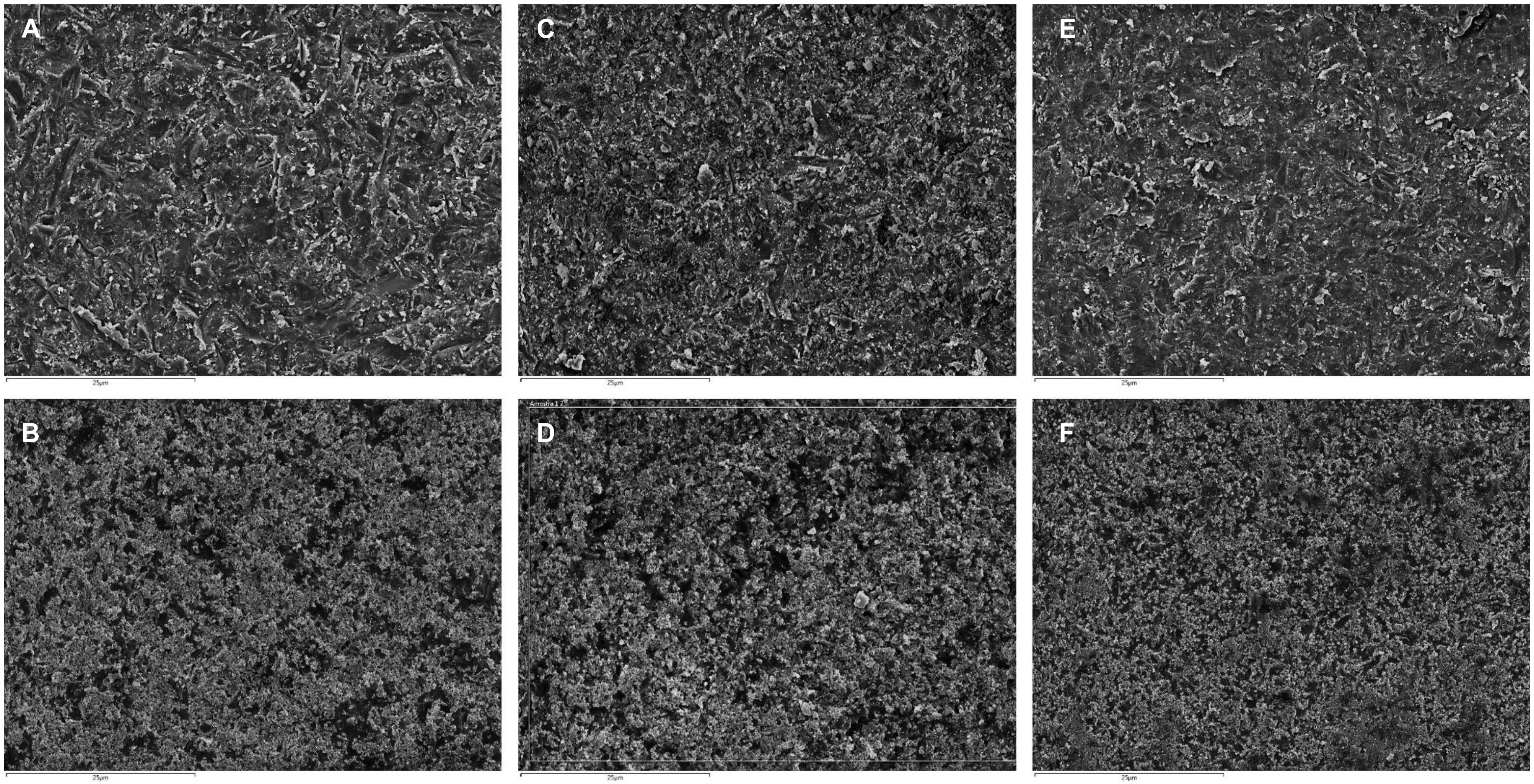

Figure 13. SEM images with 2000x magnification: A and B. Group 1 before and after cleaning procedures, respectively; C and D. Group 3 before and after cleaning procedures, respectively; E and F. Group 4 before and after cleaning procedures, respectively;

4. Discussion

From all ceramic core materials, Y-TZP ceramic stands out due to its high biocompatibility, high radiopacity, which improves the radiographic assessment of marginal integrity, and reduced core thickness because of its superior strength properties[8,9,12]. Its transformation toughening feature enables zirconia surface to counteract with external stresses, allowing to reach higher values of flexural strength, between 700 and 1200 MPa[8,63]. The combination of this active crack resistance and a high fracture resistance of more than 2,000N [8] hamper the creation of microroughness on zirconia surface. For this reason zirconia bonding procedures are very challenging because long-term high adhesion values can only be achieved when there's a balance between chemical and micromechanical bonding. Although an acidic phosphate monomer (10-MDP) was reported to create Van der Waals and Hydrogen bonds directly to hydroxyl groups from metal oxide surfaces [41], its chemical bond to zirconia surface was useless to prevent spontaneous bonding or decrease in bond strengths after long-term storage and artificial aging procedures, without surface pretreatment with air abrasion[16,25,32,41,54,64,65]

Structural defects, such as microcracks and pores, are suggested as being initiating factors of all-ceramic FDPs failures[66]. All zirconia surface roughening methods increase these pre-existing defects resulting in the occurrence of tetragonal to monoclinic complex phase transformation[11,22,23]. The consequent increase of volume of the latter phase creates compressive stresses on cracks and surface flaws, which leads to an increase of zirconia flexural strength[11]. Despite of this described event, there's a conflict between researchers, as these external stresses may lead to an increase of zirconia fatigue and a decrease in long-term fracture resistance[9,21].

Although many surface treatments have already been researched with the goal of improving bond strengths to zirconia, most of them are more aggressive and cause higher flaws in zirconia surfaces when compared to airborne-particle abrasion, such as grinding with diamond burs [21,67] or pretreat with laser instruments[51,52]. Other roughness procedures, like Selective Infiltration Etching, successfully increased bond strength to zirconia in a laboratorial environment [31,33,34], but are not viable for clinical use, for example, in case of a zirconia direct composite resin repair. For its simplicity of handling, price, results and clinical applicability, airborne-particle abrasion seems to have the most favorable risk-benefit ratio between all of the studied roughening procedures.

Despite of being an easy-to-use procedure, air abrasion has many variables, such as blasting time[60] and pressure, airborne particle composition and size[25,28,29,40,60,68] and distance of the sandblasting instrument of the surface that it's being treated. Although these variables have already been studied, inclination of the air abrasion instrument is still being left apart. This study proposed to assess and include the analysis of the effect of the latter factor, in the roughness of the zirconia surface.

In order to reduce biases and variables, distance of the sandblasting instrument, blasting pressure and time were maintained constant through all air abrasion protocols. The most studied values of distance (10mm to the surface[16,40,49,57,60,68–70]), size particles (30µm for the Cojet™ sand [16,29,40,49,60] and 50µm for the alumina particles sand[29,57,60,68,71]), blasting time (15s [16,49,57,60]), and the recommended values of pressure (2,5 bar[25,29,57,69]) were used.

Current study used 50µm alumina particles and 30µm Cojet™ sand as control groups for the new and experimental 82µm zirconia and alumina particles abrasive. Although the former two abrasives have already been intensively studied [16,29,40,49,57,60,68,71], there are still several disadvantages inherent to these particles: levels and patterns of roughness created in zirconia surface could be better and there is a considerable phase transformation from tetragonal to monoclinic while sandblasting with these particles[15]. This new abrasive with alumina and zirconia particles was suggested in the attempt of assessing its roughening capacities, in order to try to discover new patterns of roughness and alternative methods that would prevent a decrease in zirconia long-term strength. This was hypothesized once half of the particles of these experimental abrasive have the same hardness as the surface to be treated.

In the present study, group 1 obtained most of all the highest quantitative values of roughness, before and after cleaning procedures (Ra, Rq, Rz and Rc parameters). Although high mean values of roughness, profile irregularities, and peak to valley heights are very important in the micromechanical properties of a surface prepared for adhesion procedures, they don't give us information about quality of the valleys and peaks. Sharpness (Rku) and distribution (Rsk) of those valleys and peaks are essential for good wettable surfaces, and thus for good bonding strengths. Most of the reviewed studies only assessed the Ra, Rq and Rz parameters of the roughened surfaces, despising parameters that give us really important data about the surface profile pattern. Although there are many studies testing shear bond strength and tensile bond strength of composite resins to zirconia using different surface pretreatments, there is a lack of a definition of the ideal surface roughness for a bonding procedure. Researchers' community is testing adhesion procedures without fully understand micromechanical roughness created in zirconia surface. In order to interpret this pilot study results, the authors of the present study propose to briefly enounce some of the characteristics of an ideal surface roughening procedure.

In order to enhance bond strength between composite resin and zirconia, roughening procedures should create a subtractive surface, with more valleys than peaks (subtractive surface with low values of Rsk), with high values of average roughness of profile (Ra), high distances between the bottom of the valleys and the top of the peaks (high Rz values), high mean heights of profile irregularities (Rc) and smooth profile roughness patterns to improve surface wettability (low values of Kurtosis parameter). The ideal roughening procedure must deposit the lowest amount of dust particles in surface and must not create microcracks and microflaws that could lead to a decrease in zirconia long-term strength. Besides, the created surface must be stable to the dust and contaminants cleaning procedures. Hereupon, we can better assess the toughness results obtained in this pilot study.

Air abrasion *per se,* is considered a surface cleaning method due to its capacity of removing contaminations from ceramic surface, leading to higher bond values[57,59]. However, sandblasting procedures can leave dust and loose particles in the treated surface. These particles may interfere in adhesion strength since they are not bonded to zirconia surface. Therefore, phosphoric acid seems to be useful to clean the formed smear layer and greasy contaminants[59,72]. Nevertheless, in tribochemically treated zirconia surfaces, silica nanoparticles don't have enough mass and kinetic energy to get impregnated in the treated surface just like in etchable ceramics. Instead, silica particles get deposited in loose clusters or in a melted-like layer in zirconia surface[29]. Phosphoric acid might not be able to remove these loose particles that can interfere in adhesion bond strength, once they are not completely adhered to the zirconia surface. These particles might lead to cohesive failures between zirconia and silica film in a long-term.

Group 1 obtained most of all the highest values of roughness for the 90º sandblasting procedures, except for the Rku parameter. However, for the 30º sandblasting procedure, group 6 reached the highest values of roughness for the same parameters. As can be seen on Figure 5, 82μm sand and 50μm aluminum oxide particles are much sharper and have bigger diameters than 30μm Cojet™ sand particles. Therefore, it could be easily predicted that groups 1, 2, 5 and 6 would produce rougher surfaces since larger and sharper particles produce rougher surfaces[29,60]. However, when comparing the groups 1 and 2 with the groups 5 and 6, it was expected that the latter groups would produce a rougher surface. This way group 1 produced the most roughened zirconia surface although they were not composed by the larger diameter abrasive particles. This phenomenon must be elucidated in future studies in order to access the reason of this unexpected event. Although groups 5 and 6 had zirconia particles with an higher hardness and strength value[63] than alumina particles[7] composing groups 1 and 2, and had larger diameter, the expected result with higher surface roughness was not observed. Therefore, it can be suggested that zirconia particles might produce different patterns of microcracks and produce different wearing values to the zirconia surface during the blasting procedure. It might also produce a different tetragonal to monoclinic phase transformation in the sandblasting impact, which can produce different long-term strength values when comparing it with only aluminum oxide air abrasion. To evaluate the latter effects of this new abrasive, the zirconia surface profile must be assessed.

The mean values of roughness for groups sandblasted with a 90º angulation were higher than the ones sandblasted with 30º inclinations before and after cleaning procedures (Table XIII). However, if we look carefully to the Table XI values, it can be noticed that groups 4 and 6 had higher values of roughness after cleaning procedures when compared to values of groups 3 and 5. Thus, groups sandblasted with Cojet™ sand and with the new abrasive particles had higher values of roughness when air abrasion was performed with a 30º angulation. More angulated air abrasion procedures might reduce the heat during the impact of the abrasives into the zirconia surface. This heat decrease would also promote a differences in the tetragonal to monoclinic transformation[21,23]. Thus, even with the reduced roughness in the case of sandblasting with aluminum oxide (group 2), increasing angulation of the sandblasting might lead to a less deleterious effect on the pretreated zirconia strength. In future studies it should be assessed the monoclinic phase transformations comparing different sandblasting angulations. It might also be suggested that with different inclinations, the needed kinetic energy to create a good adhered silica layer to zirconia might possibly decrease. The activation of the zirconia surface, with an increase of hydroxyl groups' availability, could also be different using different angulations.

Although groups 5 and 6 had higher values of Rsk after the cleaning procedure, the values of Rku decreased. An explanation for this might be the cleaning of the dust particles that were at the bottom of the valleys. Thus, the scanned value of the height of the valleys was higher after the cleaning protocol. However, exposing the true height of the valleys in zirconia surface might gave another pattern of profile curves, increasing Rku values. Contrary to what happened to groups sandblasted with the new experimental abrasive, Rsk values decreased for groups 1, 2, 3 and 4 (Table XI). This might suggest that a different event occurred in these groups: the dust and contaminants were creating the positive "pseudo-valleys" that were etch-and-rinsed with the washing procedures.

Group 4 obtained the highest values of roughness for the 30º procedure before cleaning methods were applied. This might be explained due to the deposition of loose silica particles in zirconia surface, that are detached of the alumina core of the Cojet™ sand during the impact to zirconia, contrary to what happens with the group 2 and 6 particles, that might impinge on the surface of zirconia and are projected on the contrary direction of the sandblasting (Figure 6). Therefore, the high values in roughness parameters for group 4 might translate a "pseudo-roughened surface", since the roughness seems to be made of loose particles of silica and not real valleys or grooves in the zirconia surface, which is in accordance to Hallmann *et al.*[29]. In group 3 and 4 SEM images can perfectly be seen the silica particles (Figure 6), proven by the silica content in the EDS analysis (Table XVII). The latter groups showed a mean of 2,5% of Silica element, compared to 0% in groups 5 and 6 and 0,25% in groups 1 and 2. Despite of all the caution maintained during all surface treatments, it is suspected that the minimal percentage of 0,5% that appeared in group 2 EDS analysis, might be due to contamination between sandblasting procedures.

Cattani Lorente *et al.* concluded that tribochemically treated zirconia cleaned with isopropanol ultrasonic bath for 10min decreased the Si content by 30% by removing deposited and loose silica particles from the zirconia surface[61]. Although it seems that this decrease in silica content can be deleterious to short-term bond strength to zirconia [15], the authors of the present study believe that eliminating those loose nano-silica particles from the zirconia surface, the long-term bond strength to zirconia will be much durable and reliable. According to Hallmann *et al.*[29], these loosely adhered silica particles lead to spontaneous debonding. Thus, eliminating these particles seems to be an essential step for creating stable bond strengths to zirconia. Although isopropanol ultrasonic baths can be useful for cleaning zirconia surfaces for cementation procedures, they can't be applied for an intraoral use. Due to this limitation of ultrasonic cleaning, and due to the importance given by the authors to the cleaning of loosely adhered silica particles, it was suggested the use hydrofluoric acid as a clinical cleaning procedure.

Hydrofluoric acid is a widely used surface treatment method to etchable ceramics – ceramics containing high percentage of a glassy matrix with a silicon dioxide phase[19]. It can react with the ceramic silica matrix, resulting in a tetrafluorosilicic acid [$H_2SiF_6(l)$] that can be rinsed off with water, exposing a micromechanically retentive surface[73]. This way, we can infer that this chemical reaction will also occur when hydrofluoric acid is used to clean the tribochemically treated zirconia surface, removing the loosely adhered silica particles. It is suggested that the hydrofluoric acid might act as a selective cleaning method of the silica particles, removing loose particles, and leaving some well and deeply adhered silica particles. If it's used a multipurpose self-etch adhesive containing 10-MDP and silane for bonding procedures, this cleaning procedure might improve adhesion values in three different ways: removing loose silica particles useless for bonding procedures, exposing zirconia surface with hydroxyl groups that can create chemical bonds to 10-MDP[41]; better adhered silica particles can create chemical bonds to silane[37]; hydrofluoric acid itself might improve adhesive capacity of zirconia surface or change its potential of free energy, increasing its wettability[27]. The suggested bonding procedure might lead to an improvement of long-term zirconia bond strength if the hydrofluoric acid leave a well adhered silica film in zirconia surface.

After the cleaning protocol with 9,6% hydrofluoric acid and 37% phosphoric acid, there was a decrease in all 6 groups mean roughness values. This decrease might be due to the elimination of the alumina dust and loosely adhered silica particles in the zirconia surface. This theory is also supported by a decrease from 2,5% to 0,7% in Si content in the EDS analysis in groups 3 and 4. After cleaning procedures, the content in Aluminum decreased in all 6 groups while the Zirconium content comparatively increased in all groups. This suggests a high cleaning effectiveness in removing alumina particles remains and thus exposing a higher area of zirconia surface. Consequently, there is an increase in Zr element in EDS analysis of all groups after cleaning protocols (Table XXIII). The morphological analysis of groups 3 and 4 (Figure 10) clearly shows a decrease in these loose particles and contaminants. The use of hydrofluoric acid seems to expose a smoother and spongy pattern in zirconia surface (lower values of Rku after cleaning), with a decrease in roughness levels.

The only parameter where Cojet™ sand really stood out was in the Kurtosis measurement (Rku). The lower the Rku values, the more rounded and less sharp are the profile peaks. In order to achieve a good wettability, surface profiles must have rounded peaks over sharp peaks, to avoid any adhesive air bubbles trapped between the surface peaks. This mechanical anchorage of the adhesive promotes stable, durable and less sensitive to degradation bonds[29]. Therefore, Rku values are extremely important to assess surface bond capacities. This way, tribochemical treatment cleaned with hydrofluoric acid can be considered a mix of a subtractive and additive method of creating surface roughness.

Comparing all groups, despite of the angulation and the type of abrasive, almost of the roughness parameters were higher before the cleaning methods. Thus, it can be suggested that dust particles, contaminants and loose nano-silica particles create a "pseudo-roughened" zirconia surface, that is composed mainly by an additive roughness with higher valleys and peaks that disappear when the cleaning procedures are performed, exposing the truly roughened surface.

The authors of the present study are pretty convinced that the increasing in Si element content in the groups 1, 2, 5 and 6 (Table XX) is due to contamination of the samples during the etch-and-rinse cleaning procedures. As already enounced in this study, when hydrofluoric acid reacts with silica, it forms a tetrafluorosilicic acid [$H_2SiF_6(l)$], which is a solution that has silica in its content. When zirconia surface was rinsed with water, the silica that was present on that solution might got trapped on the roughness of the other samples that weren't sandblasted by silica-coated alumina particles. Thus, increasing the values of EDS analysis of Si element in these groups, leading to deceptive values.

Another interesting finding in this study was the presented event in Figure 4. Heterogeneous treated areas, and a common random tracing made by the acid container tip on zirconia treated surface after cleaning procedures makes suspect that the performed sandblasting procedures are not very stable. Thus, it seems that these surface treatments fail in one of the most important previously enounced feature – enable a stable roughened surface. If a simple tip of the acid container can easily produce a pronounced risk in the treated area, it means that these surface are very susceptible to external management and that the created roughened area might be poorly adhered to zirconia. Therefore, these surfaces, if not handled carefully, might fail creating long-term adhesion.

5. Conclusions

In the present study, all samples presented a decrease in surface roughness after acidic cleaning procedures. Through the SEM and EDS analysis it is suggested that cleaning with 9,6% hydrofluoric acid and 37% phosphoric acid effectively decreased loose particles and contaminants from the treated zirconia surface, with a potential benefit for bonding procedures.

Sandblasting with 50µm alumina particles with an angle of 90º created the highest values of roughness. However, samples sandblasted with 30µm silica-coated alumina and with 82µm alumina and zirconia particles showed higher values of roughness in 30º air abrasion procedures after cleaning protocols. The effect of sandblasting inclinations in zirconia surface is still unknown, but the results obtained open a new investigation interest in this area.

EDS analysis confirmed the presence of silica in zirconia surfaces that were sandblasted with silica-coated alumina particles, even after cleaning protocols. This fact can be beneficial to future chemical interaction with adhesive components, if these particles are well adhered to zirconia surface.

Results suggested that the experimental 82µm alumina and zirconia abrasive might produce an appropriate roughness, without leaving a great amount of dust after the air abrasion protocol. These new abrasive particles seem to be promising. The percentage of each component in the powder, and the inclusion of new components like silica, could be optimized to achieve a more effective and useful abrasive material.

Further studies are needed to fully understand zirconia surface behaviour to roughening procedures, and also to perform adhesion tests, once they are the reason of this basic procedure.

6. Future Researches

As a pilot study, this research resulted in some important considerations for the planning of future investigations in this field.

The obvious limitation of this study, its lack of a statistical sample, can be easily overcome. In order to conclude some assumptions that were made in this study, it's imperative to increase the number of samples.

Another limitation might be the light polish of samples in the beginning of laboratorial procedure tests. The two extensively studied abrasive powders (50µm alumina and 30µm silica-coated alumina) were used as control groups, since this was a comparative study. Although in a clinical situation, for example in a clinical veneer repair, the zirconia core that we must treat isn't as polished as in laboratory conditions, in this research it would have been useful to increase the polish to accentuate the differences between the abrasives studied.

An important question that arises after the conclusion of this study is: what is the most crucial surface roughness factor for high bond strengths? Quantitative matters? Are high roughened surface patterns, with high peaks and valleys, more important than patterns that enable a better wettability for the adhesive material? In order to ascertain these questions, future studies can assess contact angle of adhesives after using different air abrasion procedures, before and after cleaning procedures.

Strength and toughness considerations are also essential to assess. The latter can be evaluated by measuring the ratio of tetragonal/monoclinic phase transformation of zirconia surface. Other important variables that can interfere in zirconia long-term success are the heat generated during airborne-particles impact. This increase in temperature can change the ratio of phase transformation. Another important factor to take into consideration is zirconia surface wear. Thus, measuring the quantity of zirconia material loss in its surface profile, after different sandblasting procedures, could be useful in the understanding of zirconia behaviour. Higher resolution SEM images would also help to better detect microflaws and microdeffects in zirconia surface.

In what concerns the new experimental abrasive, new ratios of Zirconia/Alumina can be investigated, once different concentrations of each material can interfere differently with surface roughening procedures. Adding silica or another active chemical component to the abrasive powder, could also bring many advantages in the future adhesion protocols.

In conclusion, we still have a long way to perfectly understand zirconia surface behaviour to different pretreatment procedures. Further studies are anxiously awaited.

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