Acid etching surface treatment of feldspathic, alumina and zirconia ceramics: a micro-morphological SEM analysis.

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Abstract

Objectives: The present study is aimed at performing a scanning electron microscope (SEM) analysis to evaluate the effect of HF on the surface of feldspathic, alumina- and zirconia-reinforced ceramics.

Materials and Methods: 45 specimens of feldspathic (n=15), alumina (n=15) and zirconia (n=15) ceramics were collected. 5 specimens of each type of ceramics were not subjected to any surface treatment and analysed with SEM as controls. The remaining 30 samples were etched with 40% hydrofluoric (HF) acid gel for 2 min and then subjected to SEM analysis. Five areas of each sample were randomly selected and photographed at 0.5, 1.5 and 7.41 K X magnifications.

Results: The SEM investigation of the acid etched specimens revealed micro-morphological changes in the surfaces of feldspathic, alumina and zirconia ceramics respectively. A self-adhesive universal resin cement is desirable to obtain durable bonding to polycrystalline ceramics.

Conclusions and Significance: The adhesion between resin cements and silanated feldspathic ceramics can guarantee a valid retention of all-ceramic restorations, whereas the adhesion between polycrystalline ceramics and dental tissues remains controversial and could lead the restoration to failure. Chemically compatible dedicated cements should be used in such cases.

Key words: ceramic, feldspathic, alumina, zirconia, acid, surface

Introduction

Several attempts have been made to develop ceramic systems without metal frameworks[1,2,3]. To date, there is an increasing range of dental ceramics allowing clinicians to combine very good esthetics with optimal mechanical properties, such as glass-infiltrated porcelain, alumina- and zirconia-reinforced ceramics [4,5,6].

Several authors have described different surface treatments to improve the adhesion of all ceramic restorations. A recent in vitro study showed that the bond strength of resin-based cements is affected by the structural characteristics of ceramics[7]. It has been well documented that creating a microretentive surface texture and silane priming are necessary to obtain a reliable bond to all ceramic restorations [8,9,10,11,12,13]. A microretentive surface texture can be obtained with either chemical or mechanical methods.

The chemical etching of traditional silica-based dental ceramics was first reported in 1983[14]. Subsequently, several etchants have been recommended for the surface treatment of all ceramic restorations. Nowadays, hydrofluoric acid (HF) solutions ranging from 2,5% to 10% applied for 2-3 minutes have proved to obtain the best adhesion[15,16]. Silanization has also been recommended[15,16].

With regard to the mechanical methods to create a retentive surface, grinding, abrasion with diamond rotary instruments and airborne particle abrasion with aluminum oxide have been described in the literature.

However, the composition and physical properties of high–strength ceramic materials, such as alumina- and zirconia-reinforced ceramics, differ substantially from those of silica-based ceramics and require alternative bonding techniques to achieve strong and reliable adhesion.

Kato[17] compared airborne particle abrasion with different acid-etching agents and found that HF acid and sulphuric acid provided the highest and most durable bond strengths. On the contrary, Awliya[18] found that airborne particle abrasion showed significantly higher bond strength on densely-sintered alumina-reinforced ceramic than acid etching with either 9.6% HF or 37% phosphoric acid, grinding with diamond rotary instruments or no treatment.

Recently, several studies were performed to investigate the mechanical properties of zirconia-reinforced ceramics[19,20] as well as the techniques to enhance the bond strength of luting cement to the ceramic surface[21,22,23,24,25,26]. Blatz et al.[21] found that conventional acid etching had no positive effect on the

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resin bond to zirconia-reinforced ceramics. Derand and Derand[22] proved that an autopolymerizing resin cement exhibited the highest bond strength regardless of the surface treatment (silica coating, airborne particle abrasion, HF etching or grinding with diamond rotary instruments), while Kern and Wegner[23] achieved a durable bond to zirconia-reinforced ceramic only by using resin composites containing phosphate monomers (MDP). Janda et al.[24] proposed the PyrosilPen Technology for surface-treating of silica, alumina and zirconia ceramic to obtain good bonding with luting agents. Bottino et al.[25] recommended tribochemical silica coating systems (i.e. Rocatec, CoJet) to increase the bond strength between resin cements and zirconia-based ceramics.

The present study is aimed at performing a scanning electron microscope (SEM) analysis to evaluate the effect of HF on the surface of feldspathic, alumina- and zirconia-reinforced ceramics.

Materials and Methods

The specimen preparation and test procedure were performed according to ISO 10477 Amendment 1. The following ceramics were used:

- Feldspathic ceramics (Noritake Super Porcelain EX-3, Noritake Co., Inc., Nagoya, Japan);
- Densely-sintered high-purity alumina ceramics (Procera AllCeram, Nobel Biocare, Goteborg, Sweden & Procera Sandvik AB, Stockholm, Sweden);
- Densely-sintered yttria-partially-stabilized zirconia (YPSZ) ceramics (LAVA Frame, 3M ESPE, Seefeld, Germany).

In accordance with ISO 10477 Amendment 1, rectangular ceramic specimens with the dimensions 20±1 mm X 10±1 mm X 2±0.5 mm were provided by the respective manufacturing companies. The feldspathic ceramics were fired and polished strictly following the manufacturer's instructions. The alumina and zirconia ceramic specimens were used for the test as received from the respective manufacturing companies. 45 specimens were used to perform the present investigation, 15 per each type of ceramics. All the specimens were stored in hermetically sealed containers until the execution of the test, in order to avoid environmental contamination of the ceramic surfaces.

5 specimens of each type of ceramics were not subjected to any surface treatment and were used as controls. These samples were sputter-coated (Emitech K 550, Emitech Ltd, AsHF acidord, Kent, UK) with a gold-platinum alloy conductive layer of approximately 30 nm and subjected to a scanning electron microscope (SEM) investigation (LEO 435 Vp, LEO Electron Microscopy Ltd, Cambridge, UK). Five areas of each sample were randomly selected and photographed at 0.5, 1.5 and 7.41 K X magnifications.

The remaining 10 specimens of each group were aggressively etched with 40% hydrofluoric (HF) acid gel for 2 min. The etching procedures were performed in a laboratory under ventilation, with operators wearing protective glasses and acid-resistant gloves. The etching gel was rinsed in a polyethylene cup; the diluted solution was neutralized using a neutralizing powder made up of calcium carbonate ($CaCO_3$) and sodium carbonate (Na_2CO_3) for 5 min and thoroughly washed for 30 s. The etched substrates were thoroughly washed with water and rinsed to remove any residual acid after etching. The ceramic surfaces were then dried with oil-free air using a dental unit syringe. The treated samples were then cleaned in an ultrasonic bath (Quantrex 90 WT, L&R Manufacturing, Inc., Kearny, NJ, USA) for 10 min and dried with oil-free air.

The samples were then prepared for the scanning electron microscope (SEM) investigation as previously described. Five areas of each sample were randomly selected and photographed at 0.5, 1.5 and 7.41 K X magnifications, in order to evaluate and compare the effects of the acid etching procedures on the different ceramic surfaces.

Results

The scanning electron microscope (SEM) evaluation of the control samples revealed different morphological surface characteristics in feldspathic, alumina and zirconia ceramics respectively. The feldspathic ceramics presented a slightly

TABLE 1

MATERIAL	CRYSTAL SIZE	DENSITY	VICKERS HARDNESS
Feldspathic ceramics	3-5 _m	4.0 g/cm^3	9.8 GPa
Alumina	1-1.5 _m	3.9 g/cm^3	10.8 GPa
Zirconia	1_m	6.0 g/cm^3	13.0 GPa

Table 1 – Physical properties of the tested materials.

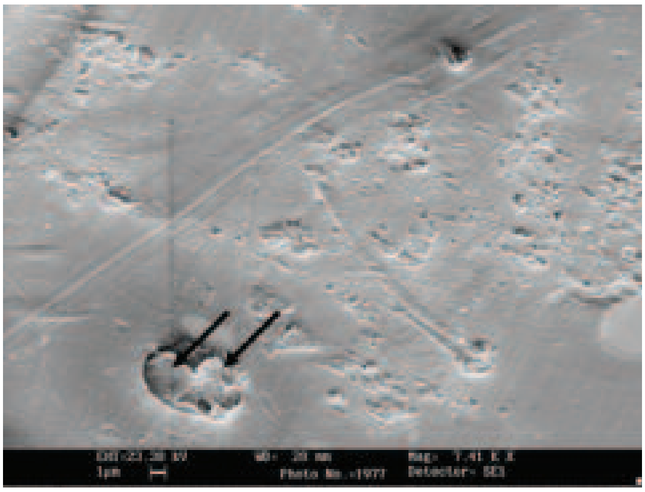

Figure 1 – Feldspathic ceramics surface before etching procedures; arrows indicate leucite crystals.

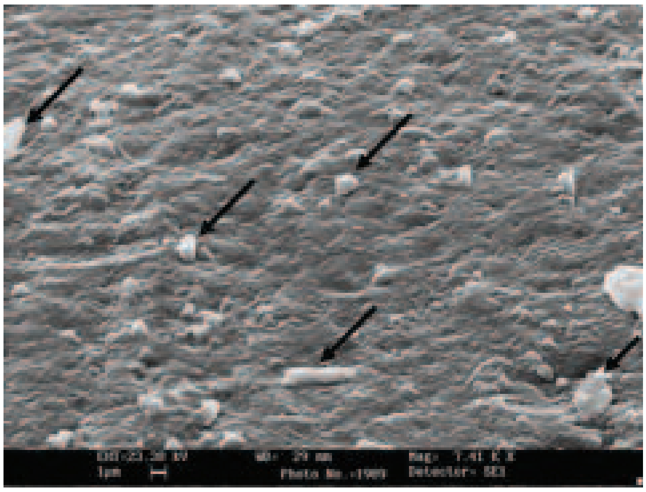

Figure 2 – High sintered pure alumina ceramics surface before etching procedures; arrows indicate alumina crystals.

irregular surface with pores and grooves of different sizes, voids and scratch-type defects (Figure 1). On the contrary, both alumina (Figure 2) and zirconia ceramics (Figure 3) showed a regular rough surface with no voids and crystals of different dimensions emerging from the ceramic surface. On the zirconia ceramic surface little groove formations were also evident (Figure 3).

The SEM investigation of the acid etched specimens revealed micro-morphological changes in the surfaces of feldspathic, alumina and zirconia ceramics respectively. A cavitation of the feldspathic ceramic surface was evident; such surface showed pores, grooves and deposition of leucite crystals, appearing as elongated structures (Figure 4). In the case of alumina ceramics, a slightly smoother superficial layer than the alumina control specimens was evident; a round-topped surface was noticed and a few little alumina crystals in the shape of irregular grains emerged from the etched surface (Figure 5). With regard to zirconia samples, the hydrofluoric acid treatment created a slightly rough dense surface; scratch-type defects were observed and zirconia crystals of different size in the shape of irregular grains lay on the surface (Figure 6).

Discussion

According to chemistry, hydrofluoric acid etching is a technique which is successful only with dental materials containing SiO_2, such as glass or SiO_2-based ceramics. High performance ceramics such as alumina and zirconia are not etched by HF acid, since they do not contain any silica phase.

In the adhesion of all-ceramic restorations, surface morphological changes, just like pores and grooves, are considered important to rheologic interlocking of resin cement to ceramics. Both micro-mechanical interlocking and the chemical bonding to the ceramic surface increase the fracture resistance of the restored tooth and the restoration; provide high retention and improve marginal adaptation, preventing microleakage. Several studies pointed out a strong corrosive effect of HF acid on dental ceramics. Consequently, HF acid is widely used in dental laboratories in conventional fixed

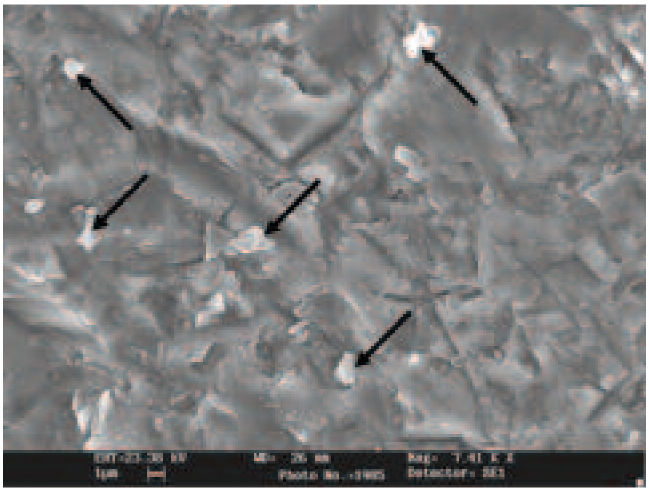

Figure 3 – High sintered yttria-partially-stabilized zirconia ceramics surface before etching procedures; arrows indicate zirconia crystals.

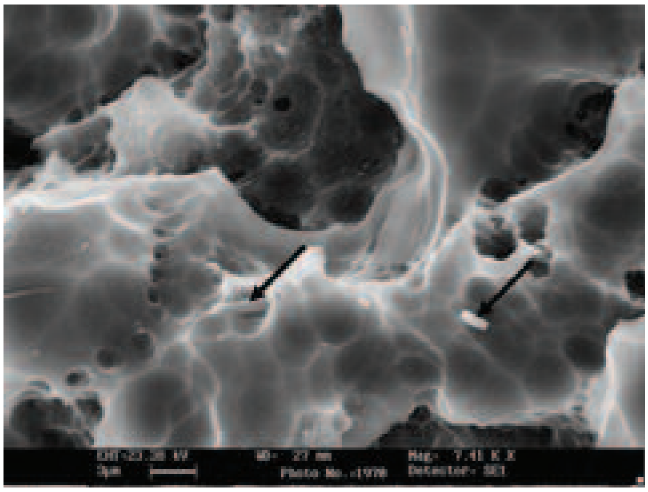

Figure 4 – Feldspathic ceramics after etching procedures; arrows indicate luecite crystals.

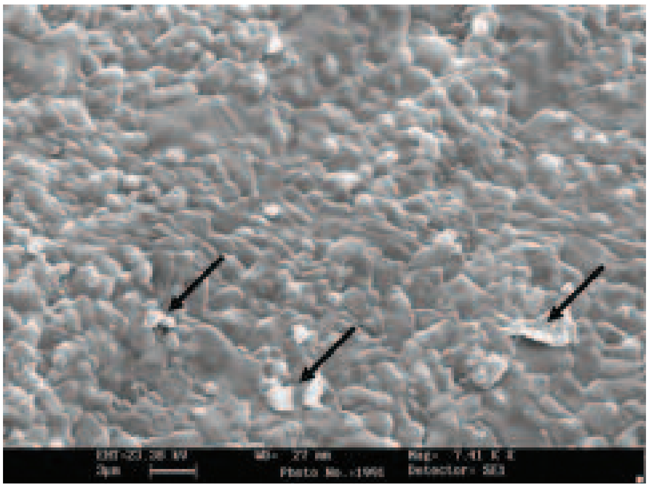

Figure 5 – High sintered pure alumina ceramics surface after etching procedures; arrows indicate alumina crystals.

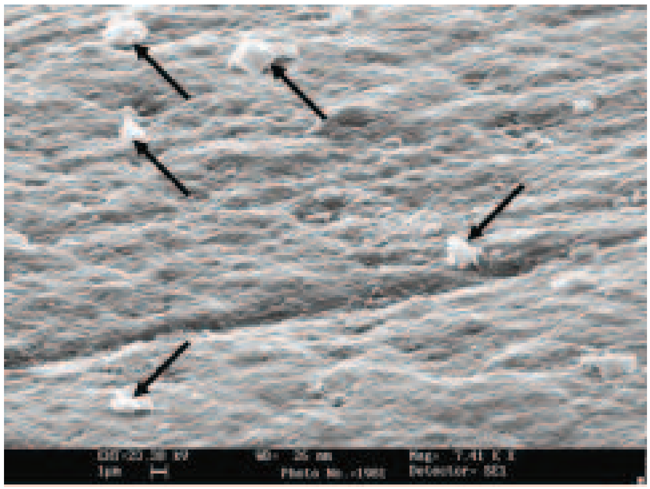

Figure 6 – High sintered yttria-partially-stabilized zirconia ceramics surface after etching procedures; arrows indicate zirconia crystals.

prosthodontics and in adhesive all-ceramic applications. The influence of the type and the concentration of the etching agent on the ceramic structure was clearly demonstrated and almost all the authors agree on the higher bond strength of HF acid-etched ceramics than that of polished or phosphoric acid-etched ceramics.

The SEM evaluation performed in the present study showed surface texture differences after the etching of feldspathic, alumina and zirconia ceramics that may influence the adhesion strength of the investigated materials to dental tissues. The surface modifications obtained by HF acid etching on feldspathic ceramic samples were not similar to the surface patterns noticed for alumina- and zirconia-based ceramic specimens (Figures 4-6). Different pore and groove dimensions were observed in etched feldspathic ceramic samples (Figure 4), whereas insufficient surface modifications were evident in both alumina (Figure 5) and zirconia ceramic specimens (Figure 6). Such a phenomenon was due to the HF acid ability of selectively removing the glassy matrix of feldspathic ceramics, exposing the crystalline structure. Conversely, the HF acid was not able to roughen the polycrystalline dense matrix of alumina and zirconia sufficiently (Figures 5 and 6). Furthermore, in comparison with feldspathic ceramics, alumina and zirconia are characterized by higher density, smaller crystal size and higher hardness (Table 1)[20,23]. Consequently, HF acid etching achieved proper surface texture and roughness only in the feldspathic ceramics samples (Figure 4).

HF acid selectively dissolved the glassy matrix of feldspathic ceramics and produced an irregular porous surface. This occurrence resulted in an increase of the surface area, which would facilitate the penetration of the luting agent into the micro-retentions of the acid etched feldspathic ceramic surface (Figure 4). Micro-mechanical retention provides the adhesion of ceramics on both enamel and dentin and several studies proved the correlation between the bond strength and the resinous tag length. The SEM investigation performed in the present study confirmed that, although a high concentration HF acid was used for a long time, the etching procedures did not sufficiently roughened the surface and did not produce a retentive surface topography on both alumina (Figure 5) and zirconia ceramic samples either (Figure 6). No micro-retentive pattern could be detected in either of the high performance sintered ceramic samples. The SEM investigation proved that since both the alumina and zirconia ceramic etched surfaces are very smooth, no micro-mechanical interlocking of the luting agent can occur.

Besides the surface conditioning methods previously described, the chemical characteristics of the luting agent play an important role in bonding to reinforced ceramics. Since adhesive cements do not directly bind to zirconia, the Rocatec treatment has been claimed to obtain effective bond strength. Nevertheless, a self-adhesive universal resin cement (RelyX Unicem, 3M ESPE) was demonstrated to reach comparable values of shear bond strength by only sandblasting the inner surface of the frameworks [26]. This cement is compatible with all types of ceramics, and is extensively used in the LAVA protocol (3M ESPE). Chemical bonding is established between the luting agent and the zirconia frames as the phosphoric groups bind the zirconium dioxide directly[26]. In the authors' clinical experience, RelyX Unicem has proved to be effective in cementing both alumina and zirconia structures. Furthermore, in a further study in preparation, the SEM investigations showed extremely limited gaps between that cement and LAVA frames (Figure 7).

Conclusions

Within the limitations of the present investigation, the results of the SEM analysis performed in this study are in compliance with data reported in scientific literature: etching with 40% HF acid for 2 min produced micro-retentions on the

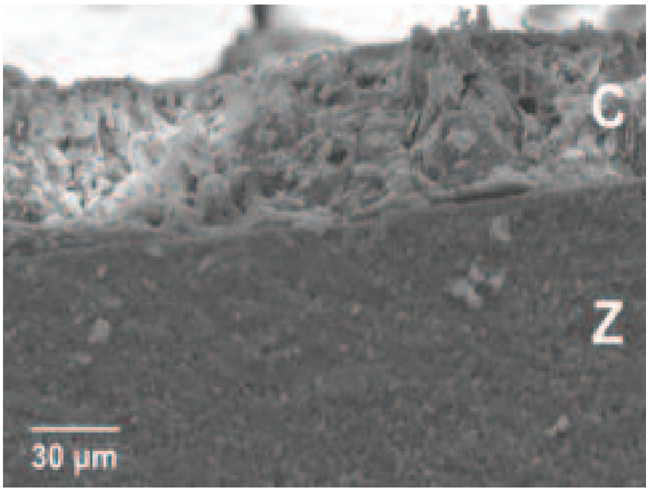

Figure 7 – Adhesive interface between a self-adhesive universal resin cement and zirconia-based ceramics (magnification: 440x).

surface of feldspathic ceramics, but did not achieve proper surface texture and roughness on both alumina and zirconia ceramics. A self-adhesive universal resin cement proved to be effective in obtaining a valid adhesion to alumina- and zirconia-based ceramics.

The clinical implications of the reported data suggest that the adhesion between resin cements and silanated feldspathic ceramics can guarantee a valid retention of all-ceramic restorations, whereas the adhesion between polycrystalline ceramics and dental tissues remains controversial and could lead to the failure of the restoration. In particular, the use of alumina and zirconia ceramics could affect the long term success of adhesively retained restorations, such as porcelain veneers; chemically compatible dedicated cements should be used in these cases.

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