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On the surface elemental composition of non-corroded and corroded dental ceramic materials *in vitro*

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Dental ceramics are traditionally looked upon as inert materials. As many are glass phased, it may be hypothesized that they will be subjected to glass corrosion in aqueous environments. The aim of the study was therefore to analyze the surface elemental composition of glass-phased and all-crystalline ceramics, before and after low- and high-intensity, *in vitro* corrosion (milli-Q-water at 37 ± 2 °C for 18 h and 4% acetic acid at 80 ± 2 °C for 18 h, respectively). The analysis of the surface elemental composition was performed using ESCA.

The hypothesis was confirmed. After high-intensity corrosion, the complete wash out of alkali ions, alkaline-earth ions and elemental alumina was found, leaving behind a surface totally dominated by silica. The all-crystalline ceramics, densely sintered alumina and yttria-partially stabilized tetragonal zirconia, displayed only minor surface changes, even after high-intensity corrosion. In comparison to the corrosion testing in acid, the corrosion process in milli-Q-water did not produce different results in principle, except for the lower magnitude of the depletion of alkali ions and the virtually unchanged level of elemental alumina. Unexpectedly, no substantial difference in surface degradation was found between the glass ceramic and the ordinary porcelain-fused-to-metal ceramic or between ceramics of higher sintering temperature and those of low or ultra-low sintering temperature. The composition and microstructure alone did not appear to provide a full explanation for the inter-individual differences in surface corrosion when exposed to comparable environmental conditions.

1. Introduction

Ceramic materials are often defined as inorganic and non-metallic materials, characterized by ionic and/or covalent bonds. The ceramic structure is based on electric neutrality [1]. With respect to the chemical composition, ceramic materials can be classified as silicate based, oxide and non-oxide ceramics. Sintered dental ceramics are mainly silicate-based ceramics, characterized by a continuous glass matrix in which different volume fractions of crystals and particles are interspersed [2]. The glass matrix in conventional ceramics is predominantly based on a potash feldspar ($K_2O\ Al_2O_3\ 6SiO_2$) and/or soda feldspar ($Na_2O\ Al_2O_3\ 6SiO_2$). During the sintering process, the feldspar forms a glassy matrix in which leucite crystal ($K_2O\ Al_2O_3\ 4SiO_2$), as well as other forms of crystals, may exist [3, 4]. In addition to feldspar, other oxides are frequently added, e.g. B_2O_3, which acts as both flux and glass former. To enhance the esthetic appearance of the ceramic material, colorant oxides of Fe, Cu, Co, Mn and opacifying oxides of Sn, Zn, Al, Zr and Ti are also added. Some of the low or ultra-low fusing dental porcelains intended for bonding to titanium and titanium alloys demonstrate compositional and microstructural differences from traditional PFM (porcelain fused to metal) porcelains [5]. The volume fraction of glass matrix is often increased and casseterite and baddeleyite crystals dominate [6]. Dental glass ceramics are polycrystalline ceramic materials, which are the result of a controlled crystallization process. They are characterized by a feldspar glassy matrix in which one or several crystalline phases are interspersed, such as tetrasilicicfluomica ($K\ Mg_{2.5}Si_4O_{10}F_2$) in the glass-ceramic Dicor, leucite ($K_2O\ Al_2O_3\ 4SiO_2$) in, e.g., the glass-ceramic Empress and mica crystals ($NaMg_3(Si3AlO_{10})F_2$) together with β spodumene crystals ($Li_2O\ Al_2O_3\ 4SiO_2$) as in Olympus

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[7]. Dental glasses, finally, are amorphous, non-crystalline and ultra-low fusing ceramic materials intended for veneering on metal or ceramic sub-structures [8].

Although they are very biocompatible, differences in composition and microstructure may result in materials of reduced hydrolytic stability. The aqueous corrosion of alkali-silicate glasses and ceramic materials with a glassy matrix is mainly an ion-exchange reaction, where alkali ions in the material are replaced by hydronium ions from the solution. The diffusion of water into surface layers results in an attack on Si–O–Si bonds, which may be successively broken [1, 9]. In principle, acidic components in the ceramic material are more resistant in an acidic environment. However, local attacks may occur due to the presence of crystalline grain boundaries, pores, phases and inclusions [10]. As an effect of the ion-exchange reactions, monovalent cations, primarily Na^+ and K^+ ions and in lithium-containing porcelains also Li^+ ions are released. Alumina and zirconia have been found to improve the durability of glasses due to the immobilization of the alkali-ions [11]. In a previous study [12], dental ceramic materials were found to demonstrate different levels of surface degradation after high-intensity corrosion. Leucite-containing ceramics generally reacted with increased surface roughness, while the contrary was true of lower crystal content materials and amorphous dental glasses.

When materials are exposed to organic substances, surface physical–chemical properties are known to influence both initial and to a varying degree, also subsequent bio-reactions [13]. Differences in protein adsorption, for example, have thus been reported to occur between metals and ceramics *in vitro* [14, 15] and, when it comes to cell and tissue responses, also *in vivo* [16, 17]. Differences in protein adsorption have even been observed between various glass materials [18] and ceramics [19] *in vitro*. It thus appears that ceramic materials may elicit different responses in a biologic environment. Since dental ceramic materials differ in both composition and microstructure, it may be hypothesized that both qualitative and quantitative differences also exist on the surface and that a corrosive environment will affect dental ceramics in a non-uniform manner. This kind of information can be retrieved by means of surface analyses of non-corroded and corroded samples.

The aim of the present study was therefore to evaluate the surface chemical composition of dental ceramics but also to evaluate possible changes in the surface composition when exposed to a corrosive environment.

2. Materials and methods

2.1. Production of test specimens

Ceramic materials with compositional and microstructural differences were selected for the experiment (Table I). From each of the sintered feldspar ceramics (Table II), ten specimens were fabricated according to the procedure described below. The ceramic specimens were fabricated using a plexiglass mold (diameter 10 mm and height 2 mm) positioned on top of platinum foil and backed by a glass slide. The porcelain powder (dentine) was mixed with an agate spatula on a glass slab using the mixing liquid recommended by the producers of each ceramic material. The mold was carefully filled with the creamy mix and condensed. Excess liquid was removed by applying a piece of adsorbent paper to the surface of the specimen. After condensation, the mold was removed, leaving the non-sintered test specimen on the platinum foil. The test specimen – still resting on the platinum foil – was transferred to a firing tray, dried in accordance with the manufacturer's instructions and

TABLE I Ceramic materials evaluated in the study

Ceramic material	Principal type	Manufacturer
Empress	Glass ceramic	Ivoclar, Schaan, Liechtenstein
Alpha	All-ceramic feldspar porcelain	Vita-Zahnfabrik, Bad Säckingen, Germany
Omega	Metal ceramic feldspar porcelain	Vita-Zahnfabrik, Bad Säckingen, Germany
LFC	Hydrothermal glass	Ducera, Rossbach, Germany
AllTitan	Ultra-low fusing ceramic for veneering on titanium	Ducera, Rossbach, Germany
AllCeram	All-ceramic mullite porcelain	Ducera, Rossbach, Germany
Denzir	Yttria-stabilized zirconia	Decim, Skellefteå, Sweden
Procera alumina core	Densely sintered alumina ($> 99.5\%$)	Procera-Sandvik, Stockholm, Sweden

TABLE II Firing schedule for the sintered ceramic materials

Ceramic	Type of firing	Starting temperature (°C)	Drying time (min)	Temperature increase (°C/min)	Vacuum (+: on −: off)	Final temp (°C)	Holding time (min)
Vita Omega	Dentine	600	6	55	+	930	1
	Glaze	600	1	110	−	930	1
Vita Alpha	Dentine	600	6	60	+	960	1
	Glaze	600	0	113.3	−	940	1
Duceram LFC	Dentine	450	8	55	+	660	1
	Glaze	450	5	55	−	650	2
Procera AllTitan	Dentine	300	7.5	55	+	725	1
	Glaze	300	5.5	55	−	710	1
Procera AllCeram	Dentine	625	6	75	+	910	1
	Glaze	625	5	75	−	890	2.5

sintered in a calibrated ceramic oven (Austromat 3001, Dekema Austromat Keramiköfen, Frilassing, Germany). The sintering was performed according to the firing schedule (Table II) and by one and the same experienced dental technician.

Before auto-glazing, the test surfaces were ground using 1000 grit (18 µm) SiC paper on a rotating disc at 150 revolutions/min under water-cooling. The test specimens were finally ultrasonically cleaned in distilled water and auto-glazed following the firing schedule. No further treatment was performed. The densely sintered alumina core specimens (Procera Sandvik, Stockholm, Sweden) were produced by compacting alumina powder in a mold, followed by sintering at a temperature of 1650 °C. After sintering, the specimens were highly polished using gradually finer grinding and polishing material, ending up with a grinding particle size of 3 µm. The glass-ceramic specimens (Empress) were produced, polished and not auto-glazed, according to the instructions of the manufacturer (Ivoclar, Schaan, Liechtenstein). The yttria-stabilized zirconia specimens (Denzir) were industrially fabricated (Saint Gobain, France) and surface finished to the same level as indicated above (Decim, Sweden). From a pool of ten specimens, four specimens were randomly chosen for the surface analyses. All the test specimens were ultrasonically cleaned in milli-Q-water (MQ water) (suprapure, distilled water) and dried in a stream of filtered compressed air. The test specimens were kept at room temperature (20 ± 1 °C) until surface elemental analysis, which was performed on the same test specimens before and after *in vitro* corrosion.

2.2. Corrosion procedure

Before starting, the polyethylene corrosion containers were cleaned by being stored in 5% HNO_3 for 48 h, rinsed repeatedly in MQ water and finally stored in MQ water for 24 h. The *in vitro* corrosion was performed in a 4% aqueous acetic acid solution, following the instructions in the ISO 6872 standards for evaluation of the hydrolytic resistance of ceramic materials [20], with minor modifications of the exposure time. According to the standards, the specimens are to be directly exposed to 4% acetic acid at a temperature of 80 °C for a time period of 16 h. To reduce the risk of micro-crack formation in the ceramics, a slower temperature increase was chosen in the present study. The temperature was therefore slowly increased from room temperature until it reached 80 ± 2 °C, increasing the total exposure time to 18 h. At a temperature of 80 °C, the rate of the degradation processes is increased, without altering the fundamental chemical reaction [21]. In order to avoid a steady-state situation at the surface of the specimens, the containers with test specimens were kept in custom-made equipment, allowing the gentle rocking of the containers during the entire corrosion procedure. To evaluate the effects of low-intensity corrosion, the corrosion procedure was repeated with another set of ceramic specimens using MQ water at 37 ± 2 °C for the same time period, i.e., 18 h.

2.3. Elemental analytical procedure

Prior to analysis, the samples were subjected to a standard cleaning procedure involving short exposure in isopropanol under ultrasonic stirring, followed by careful drying in air. This proved to be necessary to ensure that the amount of surface contamination of hydrocarbons, for example, that always appear on metallic and ceramic samples of all types was minimized. The analyses were conducted using ESCA (Electronic Spectroscopic for Chemical Analysis) with a PHI 5500 instrument (Physical Electronics, USA). The X-ray beam consisted of mono-chromatized AlK_α-radiation (energy $h\nu = 1487\,eV$), the pass energy was fixed at 93.9 eV and the analyzed areas were about $0.8 \times 2\,mm^2$. For each sample, a survey spectrum of the binding energy range of 0–1350 eV was recorded for 44 min on the horizontally mounted samples. The angle between the sample surface and the analyzer (the take-off angle), as well as that between the sample surface and the incoming X-ray beam, was then 45°. From the spectrum, the characteristic peaks of elements present in the surface were identified and the apparent elemental surface composition was derived from the peak intensities using PHI Access evaluation software and the standard relative sensitivity given therein by the equipment manufacturer [22]. Before doing this, carbon was excluded from the calculations, as this element arises from external contaminants (see above comment). A survey spectrum was taken from the central area of two randomly selected specimens of each ceramic material and was repeated after high- and low-intensity corrosion using the same specimens. The range and mean values (in atom%) were registered. In order to evaluate the degree of intra-individual compositional heterogeneity, one ceramic material was randomly chosen for ESCA elemental analysis of different surface regions before and after high-intensity *in vitro* corrosion (Table III).

3. Results

In order to illustrate the information acquired from ESCA analyses of the dental ceramics studied and to demonstrate how changes in surface elemental composition can be traced, ESCA survey spectra recorded in typical cases from an ''Omega'' sample are shown in Fig. 1. The figure illustrates the surface composition of this ceramic in the native condition (a), after corrosion in water (b) and in acetic acid (c), respectively. The identities of the characteristic peaks along the binding energy scale are displayed at the top of Fig. 1(a). In the ESCA spectrum of the non-corroded surface, strong characteristic peaks representing Na, Ba, O, K, C and Si are found. Furthermore, the presence of Sn, Ca, S and Al is also significant. All the elements that are present, apart from C, are associated with the surface condition of the Omega ceramic before corrosion testing. The presence of S and Sn was, however, unexpected in view of the manufacturer's information. As pointed out in Section 2, the C peak found before (Fig. 1(a)) and after corrosion testing (Fig. 1(b),(c)) is typical of the hydrocarbon contamination that occurs on all types of material. The intensity of the C peak also varied in an inconsistent manner when comparing different samples, probably

TABLE III Surface elemental composition in atomic % of three different regions of a single untreated and corroded dental feldspar ceramic specimen, determined by ESCA (45°; pass energy: 93 900 eV; Aperture: 5 Al 350 W; Source: monochromated)

	Untreated			Corroded	
Element	Area I	Area II	Area III	Area IV	Area V
O	51.8	53.7	53.7	62.1	62.5
C	22.5	20.2	19.1	12.2	12.0
Si	17.0	17.0	18.0	24.8	24.7
Al	4.9	4.8	5.0	0	0
K	1.3	1.4	1.4	0	0
Na	0.9	1.0	1.2	0	0
N	0.7	0.5	0.7	0.8	0.7
Ca	0.4	0.3	0.4	0	0
Ba	0.2	0.3	0.3	0	0

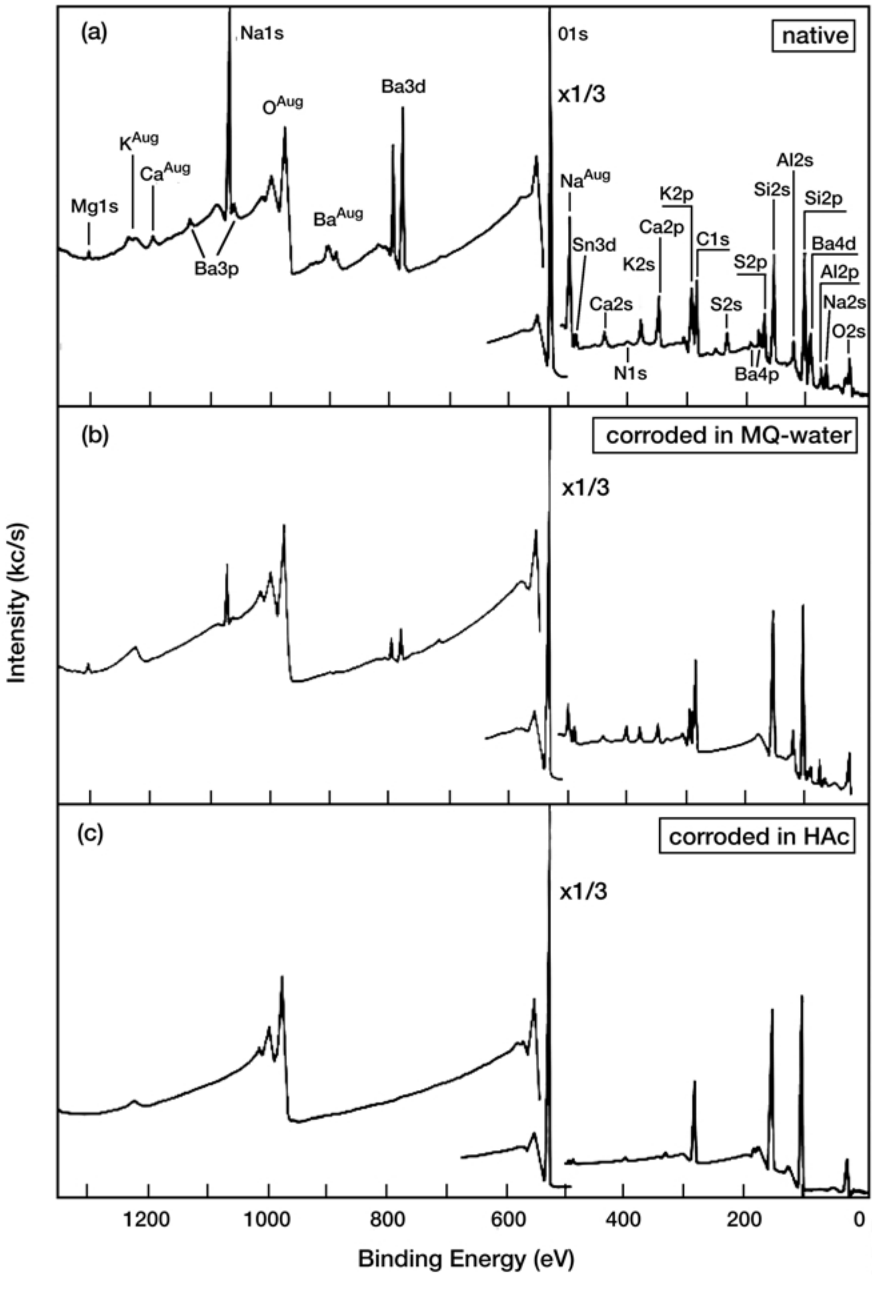

Figure 1 ESCA spectra of a dental feldspar, glass-phased ceramic (Omega) in different environmental conditions. (a) native, (b) low-intensity-corroded in milli-Q-water at 37 ± 2 °C for 18 h and (c) high-intensity-corroded in 4% acetic acid at 80 ± 2 °C for 18 h.

indicating a varying level of hydrocarbon contamination on the surface. For these reasons, disregarding the C signal in the analyses was considered justified.

When comparing the spectra in Fig. 1(a)–(c), changes in surface composition, that follow from corrosion in water and acetic acid can be identified. First, the intensities of the peaks representing Na, Ba and K are significantly lower, where the more aggressive environment – acetic acid – leads to the largest decrease in these peaks. Obviously, increasing amounts of K, Na, Ba, Ca

TABLE IV The major surface elements of various dental ceramic materials (in atom %) before corrosion (N), after corrosion in milli-Q-water (Cw) at 37 °C for 18 h and after corrosion in 4% acetic acid at 80 °C for 18 h (Ca) determined by ESCA. The blanks indicate not detected elements

Element and conditioning		Mean value and range							
		Empress	Alpha	Omega	LFC	AllTitan	AllCeram	Denzir	Alumina core
Si	N	18.0 ± 0.4	22.8 ± 0.4	19.3 ± 1.4	20.8 ± 0.5	22.2 ± 0.5	24.5 ± 0.4	0.9 ± 0.2	0.4 ± 0.1
	Cw	20.8 ± 0.2	23.8 ± 0.4	23.2 ± 0.2	22.2 ± 0.0	23.6 ± 0.6	26.9 ± 0.1	1.3 ± 1.1	0.4 ± 0.1
	Ca	28.5 ± 0.2	27.7 ± 0.2	28.4 ± 0.1	28.6 ± 0.0	27.7 ± 0.2	27.0 ± 0.1	0.3 ± 0.1	0.3 ± 0.0
Al	N	5.7 ± 0.2	5.3 ± 0.1	4.2 ± 0.6	3.8 ± 0.1	2.2 ± 0.2	3.0 ± 01		35.2 ± 0.6
	Cw	7.8 ± 0.3	4.9 ± 0.1	4.8 ± 0.4	4.3 ± 0.2	2.2 ± 0.2	3.3 ± 0.1	0.4 ± 0.1	35.7 ± 0.1
	Ca	0.3 ± 0.0	1.0 ± 0.1	0.5 ± 0.2			2.3 ± 0.0		34.3 ± 0.1
K	N	3.7 ± 0.3	3.4 ± 0.2	2.7 ± 0.3	4.0 ± 0.4	3.0 ± 0.1	2.7 ± 0.2		
	Cw	0.9 ± 0.0	1.1 ± 0.0	1.2 ± 0.1	2.0 ± 0.1	1.1 ± 0.1	1.0 ± 0.1		
	Ca		0.1 ± 0.0				0.2 ± 0.0		
Ca	N	1.9 ± 0.6	0.4 ± 0.1	1.7 ± 0.1	0.6 ± 0.1	0.1 ± 0.1	0.2 ± 0.1		0.5 ± 0.2
	Cw	0.3 ± 0.0	0.2 ± 0.0	0.7 ± 0.0	1.0 ± 0.1	0.1 ± 0.0	0.1 ± 0.0		0.5 ± 0.2
	Ca		0.1 ± 0.0				0.2 ± 0.0		0.3 ± 0.1
Na	N	2.0 ± 0.6	3.5 ± 0.7	4.2 ± 1.5	4.11 ± 0.6	3.1 ± 0.5	4.2 ± 0.8	1.8 ± 0.4	0.3 ± 0.0
	Cw	0.3 ± 0.0	0.4 ± 0.0	0.9 ± 0.4	1.4 ± 0.1	0.7 ± 0.0	0.6 ± 0.0		
	Ca								
O	N	65.5 ± 0.3	62.5 ± 1.5	63.8 ± 0.6	64.3 ± 0.2	67.8 ± 1.0	67.8 ± 1.0	67.8 ± 0.9	62.3 ± 0.4
	Cw	66.9 ± 0.3	66.0 ± 0.4	67.1 ± 0.0	67.5 ± 0.2	69.8 ± 0.2	66.7 ± 0.1	68.6 ± 0.1	63.1 ± 0.2
	Ca	70.6 ± 0.0	70.0 ± 0.2	70.4 ± 0.2	71.1 ± 0.0	71.6 ± 0.4	68.1 ± 0.1	68.9 ± 0.2	63.3 ± 0.1
N	N	2.3 ± 0.8	0.8 ± 0.4	0.8 ± 0.9	0.6 ± 0.2	0.2 ± 0.1	0.5 ± 0.2	2.2 ± 0.5	0.5 ± 0.2
	Cw	2.6 ± 0.1	2.2 ± 0.3	1.4 ± 0.2	0.7 ± 0.2	1.1 ± 0.0	1.4 ± 0.1	1.9 ± 0.0	0.5 ± 0.1
	Ca	0.6 ± 0.2	1.0 ± 0.4	0.5 ± 0.0	0.2 ± 0.0	0.4 ± 0.1	1.7 ± 0.1	1.7 ± 0.5	0.5 ± 0.2
Zr	N							24.8 ± 1.1	
	Cw			0.1 ± 0.0				26.0 ± 0.3	
	Ca				0.1 ± 0.0			24.7 ± 0.4	
Y	N				0.1 ± 0.0			1.6 ± 0.1	
	Cw							1.5 ± 0.1	
	Ca							1.5 ± 0.1	

and Al are leached from the surface as the aggressiveness of the corrosion tests increases. Second, the elements Sn, S and Mg, found at small levels on the surface before corrosion, disappear either directly during exposure to MQ water or during exposure to acetic acid. These elements are apparently enriched on the surface and contained in surface compounds or phases that can be dissolved in a corrosive environment. The same analyses as illustrated in Fig. 1 were carried out on all the samples. From these analyses, the surface elemental composition (atom %) was derived from the peak area intensities modified with the elemental sensitivity factors. In Tables IV and V, the results obtained in this manner are presented. It should be noted that the atomic percentage figures in the table are semi-quantitative and at best represent a relative accuracy of about ± 20% with respect to the true surface elemental composition. Nevertheless, the surface elemental composition of the native samples corresponds as a whole with information from the manufacturers and there are clear and consistent differences in surface composition between the different samples. Only surface elemental composition is referred to in this study and the relative content of the elements appearing as cations are taken as direct evidence of the respective compounds. So according to Table IV, the surface composition of the different glass-phased feldspar ceramics in their non-corroded state was then found to be dominated by silicon, aluminum and the alkalis, while the major components of the all-crystalline, oxide ceramics were found to be aluminum (Alumina core) and zirconium (Denzir). Additionally, lower-content components including Mg (for Empress, Omega, LFC, AllTitan, Denzir and Alumina core), B (mainly LFC), F (for Empress and LFC), Y (for Denzir) and, unexpectedly, the presence of S (mainly Omega) were found (Table V). The dramatic change in the surface elemental composition of the Omega ceramic when exposed to corrosion testing in water or acetic acid was typical of all glass-phased feldspar ceramics. Clearly, after high-intensity corrosion in a 4% acetic acid solution at 80 °C for 18 h, the complete wash-out of alkali ions K, Na, Ca and elemental alumina was found for these ceramics, leaving a surface totally dominated by silicon (Table IV). In contrast, the alumina-core veneering ceramic, AllCeram, displayed only a minor reduction in alumina (decrease in Al from 3 to 2.3 atom %). Overall surface silicon and oxygen concentrations increased after corrosion – the acid producing the largest increase. In comparison to the corrosion testing in acetic acid, the corrosion process in MQ water did not produce different results in principle, except for the magnitude of the depletion of alkali ions and the result for the level of elemental alumina, which remained unchanged or, even increased slightly. Most probably, this difference can be attributed to the fact that acidic conditions are needed to generate the hydrolysis of alumina in combination with elevated temperature (80 °C), while the alkali can be leached at a near neutral pH. When comparing the different alkali ions, it can also be seen that the surface content of sodium (Na) was stronger, even after the low-intensity corrosion testing in MQ water, whereas potassium (K) displayed a lower degree of surface depletion after this treatment. Corrosion-induced changes in minority components

TABLE V The minor surface elements of various dental ceramic materials (in atom %) before corrosion (N), after corrosion in milli-Q-water (Cw) at 37 °C for 18 h and after corrosion in 4% acetic acid at 80 °C for 18 h (Ca) determined by ESCA. The blanks indicate not detected elements

Element and conditioning		Mean value and range							
		Empress	Alpha	Omega	LFC	AllTitan	AllCeram	Denzir	Alumina core
Ti	N				0.3 ± 0.0				
	Cw				0.3 ± 0.0				
	Ca	0.1 ± 0.0			0.1 ± 0.0				
F	N	0.2 ± 0.0			0.5 ± 0.1				
	Cw				0.4 ± 0.1				
	Ca		0.2 ± 0.1			0.2 ± 0.1			
Ba	N	0.1 ± 0.0		1.0 ± 0.4		0.4 ± 0.0			
	Cw	0.1 ± 0.0		0.3 ± 0.1		0.3 ± 0.0			
	Ca								
B	N		1.6 ± 0.3		0.7 ± 0.1				
	Cw		1.4 ± 0.2						
	Ca								
Sb	N					0.6 ± 0.1			
	Cw					0.6 ± 0.2			
	Ca								
Mg	N	0.5 ± 0.1		0.2 ± 0.1	0.3 ± 0.1	0.2 ± 0.0		0.2 ± 0.1	0.3 ± 0.1
	Cw			0.2 ± 0.1			0.1 ± 0.0		
	Ca						0.1 ± 0.0	0.2 ± 0.1	0.3 ± 0.1
Zn	N				0.1 ± 0.0			0.6 ± 0.2	0.1 ± 0.1
	Cw								
	Ca								
P	N								
	Cw	0.5 ± 0.1						0.3 ± 0.0	0.2 ± 0.0
	Ca							2.8 ± 0.2	1.1 ± 0.1
S	N			2.6 ± 0.3		0.2 ± 0.0	0.7 ± 0.2		0.2 ± 0.1
	Cw								
	Ca								

(such as Mg, B and Ba) were also traceable for some materials, as indicated in Table V.

When it comes to the densely sintered ceramics, both the alumina (Alumina core) and the yttria-stabilized zirconia (Denzir) displayed only minor changes in the surface elemental composition as an effect of the exposure in 4% acetic acid (Tables IV and V). Obviously, these ceramics appeared to be resistant to this high-intensity corrosive environment. However, the zirconia showed evidence of small amounts of silicon (Si) and alkali (Na) in the surface layer and the alkali disappearance after the acetic acid exposure was typical. Moreover, after this exposure, both the oxide ceramics demonstrated increased surface content of phosphorus, an element not found in the surface of the non-corroded specimens.

The surface compositions of the ceramics as determined by ESCA were found to differ from the manufacturers' data (only pooled data for proprietary reasons, Table VI), and this applied specifically to Al, Na, K and Ca. No systematic tendency in the deviations was noted. Certain elements such as Li in AllTitan and in LFC were not detected in the ESCA spectra. It was stated in the manufacturers' list of contents that both Alpha and AllTitan should contain 1.6 atom % of boron. However, boron was only observed in the ESCA spectrum of Alpha, partly because of the difficulty involved in detecting small quantities of B when Ba is present due to interference between the only recordable B peak (B $1s_{1/2}$) at ~ 190 eV and the Ba $4p_{1/2}$ peak close to this position. In general, however, when considering the best possible accuracy (± 20%) of the ESCA results is taken into account, there is in fact a reasonable correlation between the overall elemental surface composition of the ground specimens, for example, and those expected from the manufacturers' list of contents.

TABLE VI Elemental composition (range and mean value in atom %) of six dental feldspar ceramics and two dental oxide ceramics according to information received from the manufacturers

Ceramic type				
Glass-phased feldspar ceramics			All-crystalline oxide ceramics	
			Al_2O_3	Y_2O_3-ZrO_2
Element	Range atom %	Mean atom %	Mean atom %	Mean atom %
O	58.4–62.3	60.6	60.0	66.4
Si	20.7–25.8	23.0		
Al	2.5–7.9	5.0	40.0	
Na	2.2–6.8	4.8		0.02
K	2.8–5.1	4.2		
Ca	0.04–0.5	0.3		
F	0.0–2.1	*		
B	0.0–1.6	*		
Li	0.0–1.3	*		
Ba	0.0–0.3	*		
Ti	0.0–0.3	*		
Zr		*		31.8
Y		*		1.9

*Not a frequently occurring element.

4. Discussion

When a material is exposed to a biologic environment, the first reactions that take place are confined to the extreme superficial layer of the material and are largely controlled by the chemical composition and microstructure of the surface [23]. The analytical method used here comprised a non-destructive technique with elemental analyses at a nanometer level, rendering it highly suitable for surface analyses. In addition to the inherent elements, due consideration must also be taken of the presence of various surface contaminants. Despite a thorough cleaning procedure before the ESCA analysis using isopropylalcohol in an ultrasonic device, a comparatively high surface carbon level was observed in the ESCA spectra with non-uniform interference on the binding energy signals of the other elements. As it is a non-inherent element of the ceramics [15], the surface carbon content was therefore disregarded in the analyses. Even so, carbon and other impurities constitute a surface film which may not only reflect unavoidable adsorption from the air and the effects of the handling procedures but may also constitute an integrated property of the specific material surface with an effect on subsequent bio-reactions [13, 24]. The highest carbon content was found on polished and not auto-glazed specimens, indicating a clear influence by the grinding and polishing materials, such as SiC abrasive paper and diamond paste. The origin of phosphorus on the surface of the oxide ceramics after acid corrosion and sulfur in certain non-corroded specimens, Omega in particular, was more difficult to identify.

Chemical analyses of ceramics are often associated with considerable unreliability due to the heterogeneous microstructure. However, using a large scan area, as in the current study ($0.8 \times 2\,\text{mm}$), the risk of non-representative analytical results was reduced. Moreover, in a preliminary study, only small-to-moderate intra- and inter-individual differences were observed when different surface areas in one of the ceramics were analyzed, indicating well-controlled specimen production. The quantification of the different elements using the ESCA instrument technique is generally impaired with an error of 10–20% [22], and more exact results can only be obtained by using standards. However, when used for mean value determination and not for elemental mapping, the semi-quantitative method used here can be regarded as adequate.

As expected, the surface composition of the different ceramics was dominated by oxygen, silicon, aluminum, sodium and potassium, i.e., the elements which constitute feldspar, the basis of dental silicate-based ceramics. Their composition can be delineated in the ternary–phase diagram K_2O-Al_2O_3-SiO_2, corresponding to the primary phase field of leucite $K_2O\ Al_2O_3\ 4SiO_2$ and mullite $3Al_2O_3\ 2SiO_2$ [25, 26]. The microstructure can be defined as a partially crystallized feldspar glass or glass ceramic with additions of opacifying and strength-promoting oxides [2]. Although qualitatively similar, the different native glass-phased ceramics displayed quantitative differences. Compared with information available from the manufacturers, the surface elemental composition determined by ESCA was found to correspond as a whole but to differ in detail. This circumstance may be interpreted as a lack of precise information from the manufacturer and/or as an effect of the specimen production, during which a concentration to the surface layers or an evaporation of certain elements from the surface layers may have taken place. Another explanation is reaction of the surface with small amounts of water at the elevated temperature during firing. The higher surface concentration of CaO in the sintered ceramics compared with the available information may thus have been a concentration effect, whereas the likewise higher surface concentration of oxygen may be attributed to the formation of surface hydroxide or carbon dioxide films – a corrosive effect of the ambient air. In addition to the major elements, a large number of different minor elements, such as magnesium, barium, boron, fluoride, lithium, titanium, zinc and antimony, were listed as components of the different ceramics. A few elements were not detected in the ESCA scans either due to interference with peaks of other elements – such as boron overlapping barium or simply due to the fact that the specific element was not available at the surface.

When exposed to an aqueous solution, dramatic but not unexpected changes were seen to take place at the surface of the different ceramics. Even though the dental feldspar ceramics are not simple sodium-silicate glasses, the materials are, nevertheless, dominated by the glassy matrix and the reactions of the primary glass network former – silica – largely controlling the degradation process. However, the type, size and amount of network modifiers, such as sodium, potassium and calcium and of the additional network formers, aluminum and zirconium, will also have a strong influence [27]. The effect of other minor-content additions on the durability of the different ceramics is largely unknown. Furthermore, the presence of crystalline phases may increase the corrosion resistance by offering more corrosion-resistant crystalline surfaces compared with the glass phase, but they will also supply grain boundaries, which is the preferential target of many corrosion processes [28]. It is proposed that a distinction should be made between ceramic materials with a hazardous spread of differently sized crystals and the ordered crystallization in glass ceramics, for example, the second of which is supposed to display higher corrosion resistance. Judging from the results of the present study of the surface elemental analysis after high- and low-intensity corrosion, no substantial differences in leaching pattern were seen between the glass ceramic (Empress) and the ordinary feldspar porcelain (Omega). Nor was it possible to discriminate between ceramics of higher-sintering temperature (e.g. Alpha or Omega) from those of ultra-low sintering temperatures (e.g. LFC or AllTitan) on the grounds of corrosion-induced elemental changes alone. After high-intensity corrosion, aluminum, an integrated component of the glass-phased ceramics, was found to be almost totally leached from the surface layers together with the alkalis, which must be interpreted as a degradation of Al–O–Si bonds. Obviously, the ascribed effect of reducing ion exchange by the immobilization of the alkali ions [29] was not specifically effective under acid conditions. As the only exception among the feldspar ceramics, AllCeram displayed a virtually unchanged surface content of Al after corrosion, a finding, which strengthens earlier observations on the high surface permanency of the same ceramic under the same corrosive conditions [12]. The presence of micro-mullite crystals ($3Al_2O_3\ 2\,SiO_2$), known for their high hydrolytic stability [3] and present in the matrix of this ceramic, will possibly increase the surface resistance to degradation.

When exposed to a corrosive environment, the ceramic surface will be hydrated as a result of the diffusion of H^+ ions into the surface. In neutral and acid solutions, as in the present study, ion-exchange reactions are known to take place [30]. Primarily Na^+, K^+ and Ca^{2+} ions but also Al^{3+} ions are leached, leaving a surface characterized by a silica-rich layer [27], which is assumed to reduce the rate of corrosion with time [31, 32]. The changes in surface elemental composition were most extensive in the high-intensity corrosion (4% acetic acid, 80 °C, 18 h), an effect of the acid pH ($pH = 2.4$) and the increased temperature (80 °C). However, the acid–base properties of the surface silicates and oxides, identified by the iso-electric point (IEP), also strongly affect the elemental dissolution. SiO_2 (quartz) and potash feldspar ($K_2O\ Al_2O\ SiO_2$) with IEPs of 2.2 and 1.6, respectively [33] will therefore be more resistant to degradation in acidic environments than formulations of higher IEP such as MgO ($IEP = 12.4$) or ZnO ($IEP = 9$). No IEP values for dental ceramics are available, probably due to the complex combination of different oxides together with the basal silicate structure. However, as the silica structure dominates the ceramic material – except for the oxide ceramics (Alumina core and Denzir) – a tentative IEP would be close to that of glass. Local variations in the IEP values are expected due to the inhomogeneous distribution of oxides in the surface. After corrosion, the different feldspar ceramics displayed less inter-individual variations in elemental composition compared with the native composition, an observation in accordance with that of Holland [27]. At low-intensity corrosion, the near neutral pH (pH 5.5–6.0) and the lower temperature (37 °C) reduced the corrosion attack on the surface, resulting in lower alkali leaching values but in principle comparable degradation reactions with the acid corrosion, in agreement with the findings of de Rijk *et al.* [21]. However, certain differences were found. Alumina content was virtually unchanged or slightly increased after corrosion, indicating a low leaching rate at this pH level and possible retention of alumina in the transformed surface gel layer. The silicon content also remained unchanged, whereas the surface content of nitrogen was higher than in the native and high-intensity corrosion condition.

The oxide ceramics differ fundamentally from the feldspar, glass-phased ceramics, in that they were almost all-crystalline, fine-grained ceramics with a minute volume fraction of glass in the grain boundary areas. The lattice of densely sintered alumina ($\alpha{-}Al_2O_3$) consists of oxygen atoms arranged in a hexagonal close packing, with aluminum ions occupying two-thirds of the available octahedral holes [34]. In addition to the major elements, aluminum and oxygen, small concentrations of additional elements such as silica, sodium, lime and nitrogen – often designated as impurities – were identified by the ESCA analysis. These elements most probably constitute small amounts of glass and/or silicate compounds located to the grain boundaries and selectively corroded when exposed to an aqueous environment [35]. In fact, the corrosion resistance of alumina has been closely related to its purity. Only very small changes in the surface elemental composition were observed as an effect of both high- and low-intensity corrosion, which is well in accordance with the common view that alumina is a very corrosion-resistant ceramic. However, contact with an aqueous environment leads to the formation of a surface-transformed layer of either amorphous or crystalline $\alpha{-}Al(OH)_3$, the first of which represents a higher solubility than the latter in acidic and basic solutions [36]. The IEP of densely sintered alumina ($\alpha{-}Al_2O_3$) has been found to vary between pH 6.7 and 9.4, while that of $\alpha{-}Al(OH)_3$ ranges from pH 5.1 to 9.4 [37, 33], the scattering of results generally attributed to metastable or impure states of the materials or to experimental difficulties [33]. The lowest solubility for alumina has been found in the pH range of 5–6, with increased values at both higher and lower pH values [38]. The insignificant changes in the surface concentration of aluminum, even under aggressive corrosion conditions, clearly demonstrate the low rate of corrosion. Although insignificant, these changes may still have implications for bio-interactions.

In addition to alumina, zirconia was also examined for possible surface changes due to corrosion. By adding stabilizing oxides such as Y_2O_3, it has been possible to produce an yttrium partially stabilized-zirconia ceramic (Y-PSZ-ceramic) with an almost total tetragonal microstructure of small grain size ($< 1\,\mu m$) and extreme strength properties and chemical stability [39]. The ESCA analysis of the dental zirconia ceramic (3 mol % Y_2O_3), equivalent to the surgical grade of zirconia ceramic, provided evidence of the presence and corrosion of primarily silicon and sodium, elements which have previously been related to an yttrium-silicate phase with probable localization at the grain boundaries [40]. The surface content of zirconium and yttrium remained virtually unchanged after both high- and low-intensity corrosion, a finding supported by Axelsson [41] among others. Contradictory to these findings, Lange *et al.* [42] and Li *et al.* [43] presented evidence of the surface depletion of yttrium in Y-TZP and yttria/zirconia-ion release in an acidic environment, respectively. Comparisons with other studies must, however, be made with caution since not only the chemical composition but also the experimental conditions may vary widely. The surface tetragonal-to-monoclinic transformation of Y-TZP, reported to take place as a result of aqueous corrosion, has mainly been demonstrated in high-temperature experiments ($> 150\,°C$). In more physiologic conditions, the aging process is very slow [44], which can also be concluded from this study. Surface changes do, however, take place. Using infrared and Raman spectroscopy, either water or OH groups have been identified on the surface of $ZrO_2 + 3\,mol\,\%\ Y_2O_3$ [45] and on $ZrO_2 + 2.66\,mol\,\%\ Y_2O_3$ [46], with the probable formation of $Zr(OH)_4$ and $Y(OH)_3$. Again the experiments were performed at temperatures of between 150 and 250 °C. Like alumina, the IEP of hydrous ZrO_2 and Y_2O_3 are high or 6.7 and 8.95, respectively [47, 48].

It is further proposed that the hydrated ZrO_2 surface will be stable at pH ranges of between 2 and 17 and offer a very high activation barrier for the diffusion of other ionic species through it [38, 49]. Like alumina, the long-term stability of zirconia ceramics is largely determined by the purity of the material [50] and the presence of water, even though the actual mechanism of degradation is still the subject of controversy [51].

When exposed to a corrosive environment, dramatic changes in surface elemental composition were seen in the feldspar ceramics, whereas the oxide ones only displayed minor changes. The experimental set-up favored ion-leaching reactions rather than Si–O–Si bond breakage, a situation which may not always exist *in vivo*. Water and acetic acid as low- and high-intensity corrosion media respectively differ from saliva and plasma in several respects and specifically in terms of the lack of proteins, which have been shown to shift the IEP to that characteristic of the adsorbate [33]. A correlation has been found between the value of the Z potential of biologic and inert glasses and the adsorption and adhesion of albumin *in vitro* [18], displaying higher specific adhesion and amount of albumin on the inert ceramics compared with the bioactive ones. In the *in vivo* situation, the corrosion process may proceed at different rates and with different compositions in the transformed surface layers than in the experimental set-up, which complicates the interpretation of the results from *in vitro* to strictly *in vivo* conditions. Nevertheless, the present experiments have demonstrated different aspects of the degradation processes, as well as differences between high- and low-intensity corrosion for the various ceramics. Furthermore, differences in principle in chemical durability have been shown to exist between glass-phased and all-crystalline, oxide ceramics, the latter demonstrating more constant surface conditions. In contact with bio-liquids like saliva and plasma, the surface of biomaterials will be instantly covered by a proteinaceous film, the properties of which will be strongly influenced by the specific character of the surface [22]. Among a multitude of influencing factors, the chemical composition appear to be the most crucial due to its influence on both surface charge and surface free energy, factors known to influence the adsorption of surface biofilms both quantitatively and qualitatively. Gross elemental changes as those demonstrated by the corroded glass-phased feldspar ceramics will no doubt influence several surface parameters, thereby also changing the conditions for protein adsorption and probably also subsequent biologic events. In this respect, even the minor content elements may be important.

5. Conclusions

Based on the results of the present study, it can be concluded that dramatic changes in the surface elemental composition take place in feldspar, glass-phased ceramics exposed to high-intensity, *in vitro* corrosion, whereas high-purity, all-crystalline and densely sintered ceramics display only minor changes in comparable environmental conditions. At low-intensity corrosion, the level of surface degradation will decrease. Contrary to the general belief, a polycrystalline glass ceramic resisted the surface degradation no better than the lower crystalline-content, glass-phased ceramics. Nor did high-sintering ceramics tend to be more surface corrosion resistant than lower-sintering ones, which emphasizes the importance of not extrapolating durability data from one ceramic to another, unless all the variables are known.

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