Surface Chemistry Effects of Topographic Modification of Titanium Dental Implant Surfaces: 1. Surface Analysis

Marco Morra, Dr Chem[1]/Clara Cassinelli, Dr Biol[1]/Giuseppe Bruzzone, MD[1]/Angelo Carpi, MD[2]/
Giuseppe Di Santi, MD[3]/Roberto Giardino, MD[4]/Milena Fini, MD[5]

Purpose: *To analyze the surface composition of 34 different commercially available titanium dental implants.* ***Materials and Methods:*** *Surface composition was evaluated by x-ray photoelectron spectroscopy (XPS). Samples were divided into 4 groups, depending on their surface topography (machined, sandblasted, acid etched, or plasma sprayed).* ***Results:*** *Statistical analysis of the data showed a clear relationship between surface composition and topography, which can be easily accounted for by the chemical effects of the surface treatment performed. On average, acid-etched and plasma-sprayed surfaces had higher titanium and lower carbon concentration than machined surfaces.* ***Discussion and Conclusion:*** *Current studies aimed at the evaluation of implants with different topography should not implicitly assume that topography is the only variable controlling the biologic response. Rather, when comparing different topographies, it should be taken into account that surface chemistry may be a variable as well.* (INT J ORAL MAXILLOFACIAL IMPLANTS 2003;18:40–45)

Key words: *dental implants, surface properties, titanium, x-ray photoelectron spectroscopy*

Modification of the surface topography of titanium dental implants to increase roughness is well known, commercially exploited, and widely investigated at the basic and applied levels.[1,2] Sandblasting, plasma spraying, and acid etching are the 3 most common approaches used by producers to alter surface topography and increase the surface area of implants. Many articles describe the outcome of specific surface topography on implant performances, either in vitro, in vivo, or in clinical trials. Boyan and Schwartz[3] recently reviewed studies on modulation of osteogenesis via implant surface design, stressing the role of surface roughness on phenotypic expression of osteoblast cells. Cooper and coworkers[4] used osteoblast cultures on titanium surfaces having different roughness as an in vitro model to study the effect of topography on mineralization. Cooper[5] and Cochran[6] investigated the clinical impact of rough surface topography to discover how the documented benefits found in vitro and in animal tests might translate into clinical applications. In particular, by comparing a series of published clinical studies, Cochran was able to show a documented clinical advantage of implants with roughened surfaces at a magnitude of advantage that is significant for patient care.[6] Other researchers failed to observe differences between smooth and roughened surfaces,[7] and the debate continues.

From a basic point of view, it is a known result of biomaterials science that the material/tissue interaction can be affected both by surface topography and

---

[1] Researcher, Nobil Bio Ricerche, Villafranca d'Asti, Italy.
[2] Professor, Department of Reproduction and Aging, University of Pisa, Italy.
[3] Private Practice, Porto Ercole, Italy.
[4] Professor and Chair of Surgical Pathophysiology, Faculty of Medicine, University of Bologna and Experimental Surgery Department, Research Institute Codivilla Putti, Rizzoli Orthopaedic Institute, Bologna, Italy.
[5] Researcher, Experimental Surgery Department, Research Institute Codivilla Putti, Rizzoli Orthopaedic Institute, Bologna, Italy.

Reprint requests: Dr Marco Morra, Nobil Bio Ricerche, Str. S. Rocco 36, 14018 Villafranca d'Asti, Italy. Fax: +390-141-941956. E-mail: mmorra@tin.it

surface chemistry.[8] Thus, the interpretation of interfacial interactions at implant surfaces in terms of topography only involves a major implicit assumption that is not clearly stated in the majority of articles on this subject: that topography is the only variable and surface chemistry is constant (or, at least, its possible variation, when sorted out according to the type of surface finish, does not affect significantly the biologic response). This implicit assumption is likely rooted in the common chemical nature of the samples tested (titanium). Yet, as reported in many articles, the surface composition of dental implants is widely variable,[9–15] and a closer control of the relationship, if any, between surface morphology and surface chemistry of titanium dental implants could be of help.

In this work, x-ray photoelectron spectroscopy (XPS) was used to evaluate the surface composition of 34 different commercially available titanium dental implants. It must be stressed that it was not the aim of this work to provide surface composition data of commercially available dental implants. This information has already been reported, and the variability of surface composition is well known and published.[9–15] Rather, the specific aim of this investigation was to show that there is a statistically significant relationship between surface topography and surface chemistry (more properly, between the latter and the kind of treatment used to obtain a given surface topography); and (in part 2 of this series[16]) that this surface chemistry variation can, per se, lead to the very same biologic effects in vitro that are generally interpreted in terms of surface topography only. As a consequence of these factors, it is suggested that the chemical analysis of surfaces of titanium implants (or of the titanium samples used in in vitro studies) should be an integral part of every study on the biologic response to roughened titanium samples or implant surfaces.

MATERIALS AND METHODS

XPS analysis was performed on the threaded part of commercially available titanium dental implants. The 34 samples analyzed were divided into 4 groups according to their surface finish: machined (m), sandblasted (s), acid etched (a), or plasma sprayed (p). For each group, the most commonly sold brands (in Italy) were chosen, obtaining a good selection of international and domestic production. The selected specimens account for more than 90% of the domestic (Italian) market and constitute a good share of the worldwide market.

Note that several samples had double treatments; for instance, the sandblasted/acid-etched surfaces. Since the interest here was in the surface composition, which is mostly dependent on the last type of treatment used, a surface of this type was included in the acid-etched group.

All of the samples were fully packaged and sterile, and packages were opened just before analysis. All of the samples were in their normal "service life"; that is, in no case had the validity date expired. All of the samples were made of commercially pure (cp) titanium (ie, no titanium-aluminum-vanadium alloy was used).

XPS Analysis

XPS, one of the main techniques for surface analysis, has been widely used to investigate the surface chemistry of titanium.[8–14] XPS analysis was performed with a Perkin-Elmer PHI 5500 ESCA system (Shelton, CT). The instrument is equipped with a monochromatic x-ray source (Al Kα anode) operating at 14 kV and 250 W. The diameter of the analyzed spot was approximately 400 µm, the base pressure was 10^{-8} Pa, the angle between the electron analyzer and the sample surface was 45 degrees, and the pass energy was 187.8 eV. Quantification of elements was accomplished using the software and sensitivity factors supplied by the manufacturer. The correctness of the sensitivity factors used was verified independently by the evaluation of lightly sputtered titanium dioxide reference samples (Sigma, Milan, Italy).

Statistical Analysis

Analysis of variance (ANOVA) was performed to compare the surface composition of the 4 groups of dental implants. Thus, the null hypothesis was that groups are not different, and ANOVA was performed to check its correctness. Student unpaired *t* tests were also performed to determine any differences between groups. More details are reported in the Results section.

RESULTS

Surface Composition Data

Results of the surface analysis of the 34 titanium dental implants tested in this study are reported in Table 1. Samples were coded by a number and the type of surface finish. Generally, these data are in agreement with published findings,[9–15] which show a number of chemical elements in addition to the expected titanium and oxygen. This topic has been treated in detail in other reports and will not be discussed here. However, most of the elements can be tracked back to cleaning and washing procedures (magnesium, sodium, calcium, chlorine, phosphorus); contact with

Table 1 Surface Composition as Detected by XPS Analysis of the 34 Implants Tested

Implant no.	Implant surface	C	O	Ti	N	Al	Si	Na	Mg	Ca	Zn	Cl	F	P
1	m	76.5	18.2	1.4	2.1		0.6		0.2	0.6		0.3		0.1
2	m	73.2	20.6	1.6	0.6		3.0	0.2	0.2	0.2		0.1	0.1	0.2
3	m	66.5	24.6	4.7	1.0		0.8	0.2		1.8		0.3		
4	m	51.1	29.5	7.6	2.2		1.9	0.5		0.2		0.9	5.5	
5	m	54.9	30.5	8.5	2.9		0.5	0.2	1.0	0.3		0.2	0.1	
6	m	51.2	33.9	10.2	1.2		1.2	0.1	0.8	0.3		1.0		
7	m	46.7	37.1	11.4	0.7		1.9	0.4		1.5	0.2	0.1		
8	m	41.9	39.4	12.3	1.7		2.1		0.2	0.2		0.3	1.6	0.3
9	m	35.5	40.8	12.7	1.8		7.0		0.9	0.5	0.2	0.5		
10	m	33.8	46.2	13.1	3.2		0.7		0.6	0.1		0.3		2.0
11	m	39.5	42.9	13.9	1.3		1.5					0.1	0.7	
12	s	47.2	31.6	3.3	1.3	14.7	1.4			0.4				
13	s	17.9	51.7	18.3	0.7	6.3	2.4			0.5			2.0	
14	s	25.7	46.5	4.6	0.6	17.5	2.9	0.6	0.6	0.8	0.2			
15	s	40.6	39.3	6.5	4.7	0.9	0.8	1.5	1.5	1.3	0.2	0.9		1.8
16	s	40.9	38.2	7.0	0.7	4.4	1.6	0.8	2.5	2.5	0.5	0.2		0.5
17	s	46.9	34.0	9.3	0.7		3.3	0.6	2.4	1.8	0.5			0.5
18	s	43.6	36.2	11.9	0.8	3.1	0.1	0.3	2.1	1.1		0.1	0.5	
19	s	35.4	44.4	14.4	1.6		0.9	0.6		0.6	0.2	0.9		1.0
20	s	20.5	51.6	14.8	1.3	9.4	1.2	0.9				0.2		
21	s	33.9	46.8	14.9	1.1		0.7	1.3	0.3	0.1		0.1	0.8	
22	a	47.0	33.5	9.4	3.5	2.4	1.2		0.8	0.7		0.6	0.8	
23	a	42.9	38.2	12.5	2.8		1.4			0.8		0.6	0.7	
24	a	26.9	48.2	15.7	1.9		2.9	1.4		0.2			1.9	1.0
25	a	36.2	43.5	15.8	1.0		2.5	0.2		0.1		0.2	0.3	
26	a	40.9	39.3	16.5	0.1		2.0			0.5				
27	a	23.5	48.9	16.5	3.8		1.8	2.9	0.3	0.3		0.3	0.9	
28	a	23.2	43.9	17.0	2.2		1.6	2.9	0.5			0.3	8.4	
29	p	49.4	32.1	11.7	5.0		0.3			0.9				0.6
30	p	33.4	42.9	15.8	4.1		1.0	0.2	0.7	0.9		0.7		
31	p	31.2	46.8	16.8	3.9		0.4			0.3		0.3		
32	p	33.5	43.5	17.1	2.3		1.8	0.9	0.9	0.1				
33	p	33.4	45.3	17.4	2.0		0.8	0.5		0.4		0.1		
34	p	29.4	48.4	18.1	2.2		0.5			0.1		0.2	0.6	0.3

m = machined; s = sandblasted; a = acid etched; p = plasma sprayed.

tools (zinc); acid pickling (nitrogen, fluorine); and sandblasting (aluminum). Carbon is the most prominent contaminant of titanium surfaces. Part of the carbon detected is the result of the unavoidable adsorption of carbon-containing atmospheric compounds to the titanium surface.[9] However, especially in the case of machined surfaces, carbon often reaches very high values, which cannot be accounted for by adsorption of airborne compounds only. Contamination by lubricating fluids and oils is the more likely explanation.

Table 2 shows means and standard deviations of the whole set of data and of the 4 different groups. Considering the overall titanium concentration (that is, the averaged value of all 34 samples), it is interesting to note that the standard deviation is slightly less than ± 50%. Clearly, when different implant surfaces are compared only on the basis of their surface topography, the assumption of identical surface chemistry should be considered carefully and not taken for granted. Acid-etched and plasma-sprayed surfaces showed, on average, a higher amount of titanium and a markedly reduced standard deviation as compared to machined surfaces.

Statistical Analysis

Figs 1 and 2 show the results of ANOVA statistical tests performed on the titanium and carbon surface concentration as detected by XPS. The figures show the obtained means of the 4 groups and the 95% confidence intervals. Clearly, the titanium concentration detected on the acid-etched and plasma-sprayed samples was higher than that

Table 2 Means and Standard Deviations of the Surface Composition Data of Table 1

Group	C	O	Ti	N	Al	Si	Na	Mg	Ca	Zn	Cl	F
All samples												
Mean	40.4	39.4	11.8	2.0	7.3	1.6	0.8	0.9	0.6	0.3	0.4	1.8
SD	13.7	8.4	4.9	1.3	6.0	1.3	0.8	0.7	0.6	0.1	0.3	2.3
m												
Mean	51.9	33.1	8.9	1.7		1.9	0.3	0.6	0.6	0.2	0.4	2.0
SD	14.7	9.2	4.5	0.8		1.8	0.2	0.4	0.6	0.0	0.3	2.4
s												
Mean	35.3	42.0	10.5	1.4	8.0	1.5	0.8	1.6	1.0	0.3	0.4	1.1
SD	10.6	7.2	5.1	1.2	6.2	1.0	0.4	0.9	0.8	0.2	0.4	0.8
a												
Mean	34.4	42.2	14.8	2.2	2.4	1.9	1.9	0.5	0.4		0.4	2.2
SD	9.8	5.6	2.8	1.3		0.6	1.3	0.3	0.3		0.2	3.1
p												
Mean	35.1	43.2	16.2	3.3		0.8	0.5	0.8	0.5		0.3	0.6
SD	7.2	5.8	2.3	1.2		0.6	0.4	0.1	0.4		0.3	

m = machined; s = sandblasted; a = acid etched; p = plasma sprayed; SD = standard deviation.

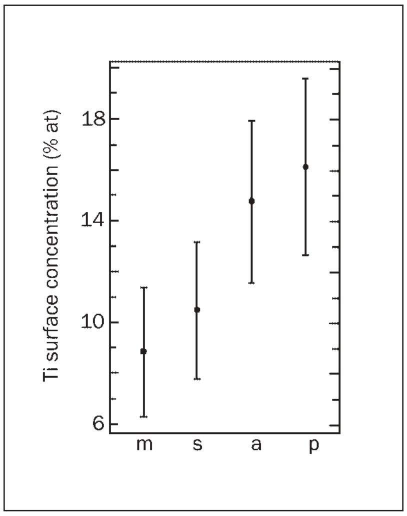

Fig 1 *(Left)* Mean surface concentration of titanium and the 95% confidence interval for means of the 4 groups of samples. m = machined; s = sandblasted; a = acid etched; p = plasma sprayed.

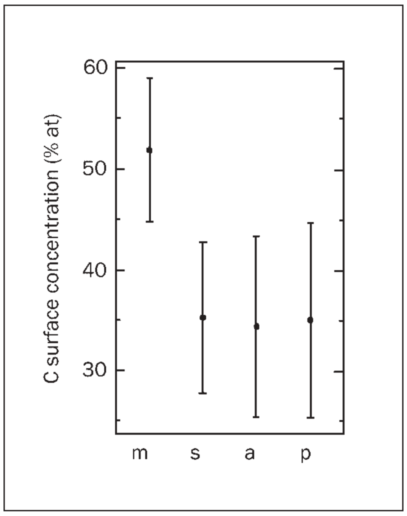

Fig 2 *(Right)* Mean surface concentration of carbon and the 95% confidence interval for means of the 4 groups of samples. m = machined; s = sandblasted; a = acid etched; p = plasma sprayed.

detected on machined surfaces. Machined surfaces showed a higher surface concentration of carbon as compared to rough surfaces. Student unpaired *t* tests were performed to determine the significance of the observed differences between groups. Relevant results are shown in Table 3.

DISCUSSION

XPS analysis has frequently been used to detect the surface composition of dental implants.[9–15] Wide variations in the concentration of the key elements and the presence of a number of unexpected elements

Table 3 Results of Student Unpaired *t* Tests Between Groups

Element/group	s	a	p
Carbon			
m	.0084**	0.14**	.020**
s		.86	.97
a			.89
Titanium			
m	.44	.0072**	.0024**
s		.063*	.023*
a			.36

*$P < .05$; **$P < .01$. Figures show the probability of each result, assuming the null hypothesis.

have been reported. Titanium is notoriously a very reactive metal, and its surface is covered by an oxide layer (TiO_2). Thus, in the surface analysis of titanium devices, the maximum theoretical amount of titanium expected is 33%, with the rest being oxygen. Adsorption of ubiquitous hydrocarbons from the atmosphere to high-energy surfaces is unavoidable under normal conditions,[9] and a significant amount of carbon is normally detected in the surface analysis of metal devices. In the case of titanium implants, this adsorption further lowers the percent titanium concentration below the theoretical limit of 33%. It was recently suggested that about 18% surface concentration of titanium is a reasonable value for clean titanium surfaces in the normal environment.[14] The implications and meaning of the carbon/titanium ratio of dental implant surfaces have been discussed previously.[9–15]

While the results of surface analysis of dental implants have been widely discussed in the literature, the specific aim of the present paper was to compare the surface concentration of dental implants that had different surface topography. The data showed that there was indeed a statistically significant difference between the groups of implants having different surface topography (Table 3). Generally, machined surfaces contained significantly more carbon and significantly less titanium than roughened surfaces (in the latter case, with the exception of sandblasted surfaces). Actually, the data of Table 1 and 2 show a very straightforward chemical rationale in the apparent confusion of the data. Machined surfaces, which obviously undergo a great deal of machining and polishing work and must face direct contact with the machining tools, contain, on average, the greatest amount of carbon, as a consequence of the contact with organic lubricating fluids.[16] The details of the cleaning routines probably play a more important role for this type of surface than, for instance, a plasma-sprayed surface. In the latter case, surfaces are intrinsically cleaner because of the nature of the finishing technique. The plasma-sprayed surface does not come into contact with machining tools or lubricating fluids, and organic contaminants are burned out at the temperature of the plasma spray.

Acid-etched samples are another interesting example; acid etching, either by hydrofluoric or hydrochloric/sulfuric acid, dissolves the outermost layers of the implant surface. The carbon content (or, better, the carbon/titanium ratio) of this class of implants is comparatively low, because etching removes, together with the outer layers of titanium, most of the carbon contaminants introduced on the surface by machining. Thus, in addition to the effect on surface topography and, as recently suggested, on cell phenotype,[3] acid etching also has a significant chemical effect. From an experimental point of view, and this is the primary result of this work, it makes the surface of the acid-etched sample used in cell culture or in in vivo tests chemically different, at the 99% confidence level (Table 3), from the surface of a smooth sample. Note that for both plasma spraying and acid etching, a significant side effect of the surface preparation routine was the reduction of the standard deviation of titanium concentration (see Table 2), which decreases to very reasonable values, as compared to machined and sandblasted surfaces. Thus, acid-etched and plasma-sprayed surfaces are not only, for obvious chemical reasons, cleaner, they are also much more reproducible than machined and sandblasted surfaces.

CONCLUSIONS

Quantitative data shown in Table 1 and 2 indicate that, even if a great deal of variation was observed in the carbon content of the different samples tested (the contribution from packaging adds to the finishing and cleaning routine), it appears that a direct relationship exists between the surface finishing and the surface carbon/titanium ratio. With respect to in vitro testing and evaluation of dental implants, recent literature includes some interesting studies on the effect of surface roughness on cell biochemistry, which have been attributed to the effect of surface topography on cell behavior.[3,4,17–19] On the other hand, the data of Table 1 suggest that surface topography and surface chemistry are inextricably bound. The information that surface spectroscopy can bring to investigators involved in in vitro testing is that, unless specifically demonstrated by surface analysis, it is not correct to assume that the surface chemistry of the same substrate (titanium) subjected to different surface-finishing procedures is the same, and that it is not that easy to make cells respond only to topography, all other parameters being the same. What must still be demonstrated is that chemical variations such as those reported in Table 1 can indeed affect biologic response, either clinically or in laboratory experiments. In vitro studies on this topic are reported in the second paper of this series.[16]

REFERENCES

1. Davies JE (ed). The Bone-Biomaterial Interface. Toronto: University of Toronto Press, 1991.
2. Davies JE (ed). Bone Engineering. Toronto: em squared, 2000.
3. Boyan BD, Schwartz Z. Modulation of osteogenesis via implant surface design. In: Davies JE (ed). Bone Engineering. Toronto: em squared, 2000:232–239.
4. Cooper LF, Masuda T, Whitson SW, Yliheikkila P, Felton DA. Formation of mineralizing osteoblast cultures on machined, titanium oxide grit-blasted, and plasma-sprayed titanium surfaces. Int J Oral Maxillofac Implants 1999;14: 37–47.
5. Cooper LF. A role for surface topography in creating and maintaining bone at titanium endosseous implants. J Prosthet Dent 2000;84:522–534.
6. Cochran DL. A comparison of endosseous dental implant surfaces. J Periodontol 1999;70:1523–1539.
7. Ratner BD. New ideas in biomaterials science—A path to engineered biomaterials. J Biomed Mater Res 1993;27: 837–850.
8. Kasemo B, Lausmaa J. Surface science aspects on inorganic biomaterials. Crit Rev Biocompatibility 1986;2:335–380.
9. Karlsson U, Gotfredsen K, Olsson C. A 2-year report on maxillary and mandibular fixed partial dentures supported by Astra Tech dental implants. A comparison of 2 implants with different surface textures. Clin Oral Implants Res 1998;9: 235–242.
10. Kasemo B, Lausmaa J. Biomaterial and implant surfaces: A surface science approach. Int J Oral Maxillofac Implants 1988;3:247–259.
11. Klauber C, Lenz LJ, Henry PJ. Oxide thickness and surface contamination of six endosseous dental implants determined by electron spectroscopy for chemical analysis: A preliminary report. Int J Oral Maxillofac Implants 1990;5:264–271.
12. Smith DC, Pilliar RM, McIntyre NS, Metson JB. Dental implant materials. II: Preparative procedures and surface spectroscopic studies. J Biomed Mater Res 1991;25:1069–1084.
13. Kasemo B, Lausmaa J. Biomaterial and implant surfaces: On the role of cleanliness, contamination and preparation procedures. J Biomed Mater Res 1988;22:145–158.
14. Morra M, Cassinelli C. Evaluation of surface contamination of titanium dental implants by LV-SEM: Comparison with XPS measurements. Surf Interf Anal 1997;25:983–988.
15. Wieland M, Sittig C, Brunette DM, Textor M, Spencer ND. Measurement and evaluation of the chemical composition and topography of titanium implant surfaces. In: Davies JE (ed). Bone Engineering. Toronto: em squared, 2000:163–181.
16. Cassinelli C, Morra M, Bruzzone G, et al. Surface chemistry effects of topographic modification of titanium dental implant surfaces. 2: In vitro experiments. Int J Oral and Maxillofac Implants 2003;18:46–52.
17. Martin JY, Schwartz Z, Hummert TW, et al. Effect of titanium surface roughness on proliferation, differentiation and protein synthesis of human osteoblast-like cells (MG63). J Biomed Mater Res 1995;29:389–401.
18. Boyan BD, Batzer R, Kieswetter K, et al. Titanium surface roughness alters responsiveness of MG-63 osteoblast-like cells to $1\alpha,25\text{-(OH)}_2D_3$. J Biomed Mater Res 1998;39:77–85.
19. Kieswetter K, Schwartz Z, Hummert TW, et al. Surface roughness modulates the local production of growth factors and cytokines by osteoblast-like MG-63 cells. J Biomed Mater Res 1996;32:55–63.