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In vitro corrosion of titanium

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Abstract

Titanium is used in dentistry for implants and frame work because of its sufficient chemical, physical and biological properties. The corrosion behaviour is from high interest to value biocompatibility. A static immersion test was undertaken with a titanium test specimen (30 mm × 10 mm × 1 mm, immersion time = 4 × 1 w, $n = 3$ for each series). The following parameters were investigated: specimen preparation, grinding, pH-value, different casting systems, comparison with CAD/CAM, influence of: chloride, thiocyanate, fluoride, lactate, citrate, oxalate, acetate. Atomic absorption spectroscopy was used to analyse the solutions weekly. The course of corrosion was investigated photometrically. Titanium reveals ion releases [(0.01–0.1) μg/(cm^2 × d)] in the magnitude of gold alloys. There is little influence of grinding and casting systems in comparison with organic acids or pH value. The ion release increases extreme (up to 500 μg/(cm^2 × d)) in the presence of fluoride. Low pH values accelerate this effect even more. Clinically, no corrosion effects were observed. Nevertheless it is recommended that it is best to avoid the presence of fluoride or to reduce contact time. In prophylactic fluoridation of teeth, a varnish should be used.

Keywords: Corrosion; Titanium; Fluoride; Organic anions; Inorganic anions; Casting systems; CAD/CAM systems

1. Introduction

Corrosion is one parameter to determine the biocompatibility of dental alloys. Titanium is known as a corrosion resistant and very biocompatable [1–4] material for dental implants [5–7] and frame work.

Nevertheless, the very complex chemistry of the oral cavity may reveal surprises concerning corrosion processes. Aim of this study was to investigate the influence of manufacturing and different anions on the corrosion of titanium.

2. Materials and methods

Test specimens (30 mm × 10 mm × 1 mm, $n = 10$) consisting of pure titanium (grade 1) were casted by several casting and one CAD/CAM system by different commercial dental laboratories and companies (Table 1). Static immersion tests were undertaken in different corrosion solutions (Table 1). The ion release was determined by atomic absorption spectroscopy. Test specimens for the investigation of the influence of different ions were made of cold formed titanium (Tikrutan RT 35/Deutsche Titangesellschaft, Tyssen, 20 mm × 30 mm × 0.5 mm, $n = 3$). All test specimens were immersed for four weeks in corrosion solution. The solutions were exchanged weekly and were analysed with atomic absorption spectroscopy (furnace technique).

3. Results

The comparison of the influence of casting and CAD/CAM systems revealed that there are more differences between the dental laboratories than between different casting systems (Fig. 1). There are no clinical relevant differences between casting and CAD/CAM systems. In each case the release of titanium is in the magnitude of the ion release from gold or cobalt–chromium alloys. The high ion releases of the Avatron system (Asahi company) exhibit, that even a poor cast (by a beginner) reveals ion releases comparable to cobalt chromium alloys.

The presence of thiocyanate ions decrease the ion release of titanium compared to chloride ions (Fig. 2).

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Table 1
Investigated casting and CAD/CAM systems and compositions of corrosion solutions

System/company	Casting or CAD/CAM system	Composition of corrosion solution (each 0.1 mol l^{-1})	Aim of investigation
Avatron/Asahi	Casting	NaCl, HLac	Casting vs. CAD/CAM
Titaniumer/Ohara	Casting	NaCl or NaF or NaSCN and HLac	Inorganic ions
Castmatic/Dentaurum	Casting	HLac or HAcor HOx or HTar and	Organic ions
Rematitan/Dentaurum	Casting	NaCl	
Cyclac/Morita	Casting	HLac = lactic acid HAc = acetic acid	Investigations with inorganic and organic ions were undertaken with Tikrutan TR 35 test specimens of Tyssen
Cowa Dental	Casting	HOx = oxalic acid HTar = tartaric acid	
Nobel pharma/Procera	CAD/CAM, sparc erosion	NaF = sodium fluoride NaCl = sodium chloride	
Cold formed/Thyssen	Cold formed	NaSCN = sodiumthiocyanate	

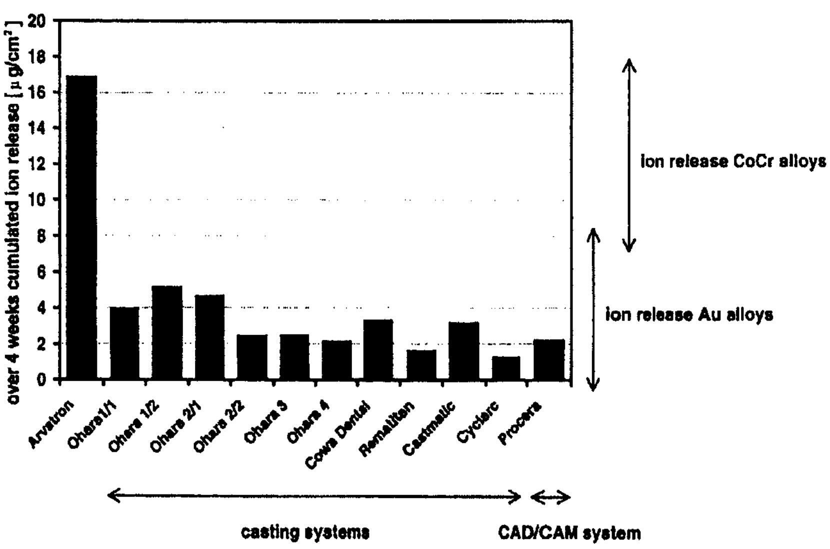

Fig. 1. Influence of different casting systems on the ion release of titanium.

Flouride ions reveal titanium releases up to 10 000 times higher. This effect is even more accelerated by the presence of other organic ions (Fig. 3). There are complex relations between organic and inorganic ions and the pH-value. A direct relation between pH-value, organic ions and ion release can only be observed in the sodium chloride containing solutions. Low pH-values increase the ion release.

Grinding of the test specimens reduces the titanium release in every case. Unground test specimens reveal approximately three times higher ion releases.

4. Discussion

Because of the extreme low ion releases corrosion is influenced almost completly by the surface. Therefore, little inhomogenous areas on the surface accelarate the ion releases. Only by the presence of fluoride ions deeper regions of the titanium are reached.

Titanium casting systems show differences in the melting procedure, mould material and investment materials [8–29]. Although the dental laboratories use different wax techniques. All those parameters lead to the observed differences. This investigation exhibit that the differences between dental laboratories using the same casting system can be larger than the differences between different casting systems or between casting systems and the investigated CAD/CAM system. Titanium exhibits a sufficient passivating behaviour which is nearly independent from the casting or CAD/CAM system. Reason for the passivation is the formation of stable oxide layers which are formed in a few nanoseconds [30].

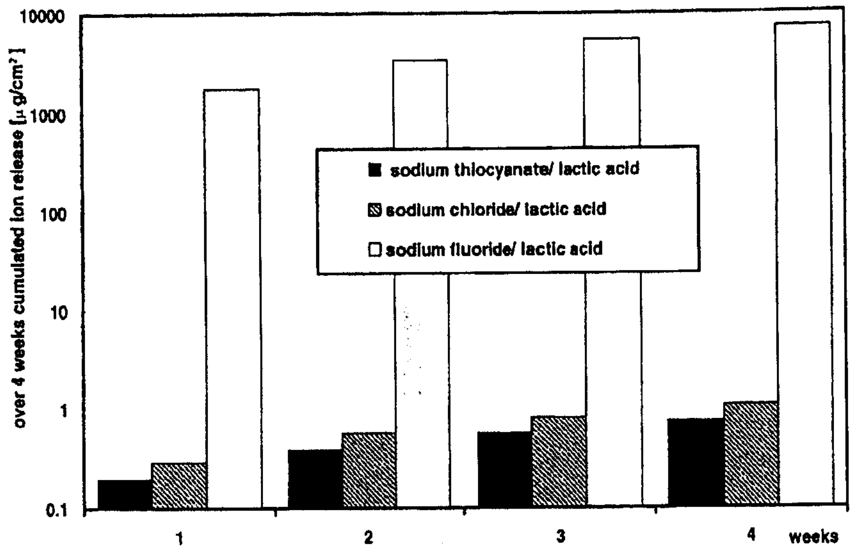

Fig. 2. Influence of chloride, thiocyanate and fluoride ions on the corrosion behaviour of titanium.

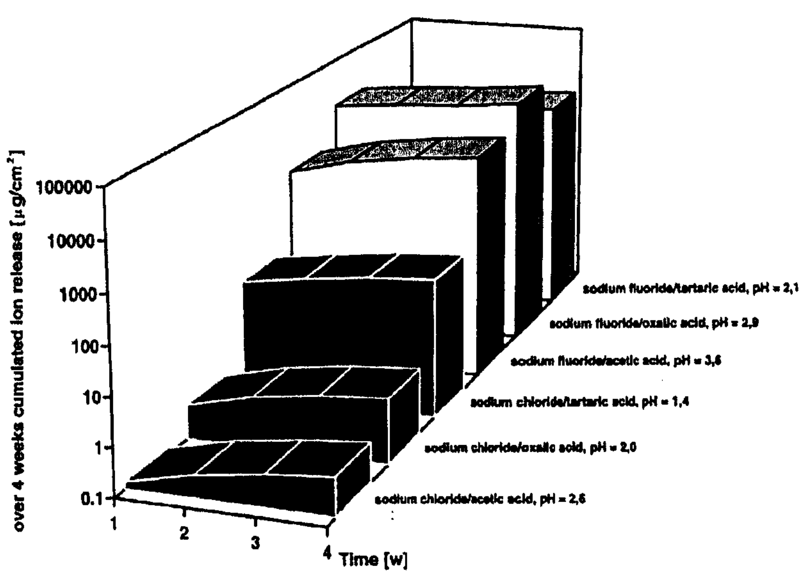

Fig. 3. Influence of lactate, acetate, oxalate or tartrate in combination with chloride or fluoride ions on the corrosion behaviour of titanium.

Fluoride containing tooth pastes or prophylactic agents can react with titanium surfaces [31–34]. On the other hand, no clinical cases are published which report changes of titanium surfaces in vivo. As reason for this the formation of biological films on the titanium surfaces can be assumed. Also, the saliva in the oral cavity dilutes the flouride concentration and functions as a buffer.

Because the concept of PEARSON of soft-acid-hard-base reactions (SAHB concept) [35] it is explicable that fluoride ions exhibit a high reactivity towards titanium in contrast to chloride and thiocyanate ions. Fluoride ions can form soluble complexes with titanium ions derived from the oxide layers. Without the passivating oxide layers acid corrosion can take place and titanium reacts like one can aspect from its position in the electrochemical series.

Because of the discussed mechanism of the solvation of the passivatig oxide layers and the accelerated solubility of titanium oxide by decreasing pH-values the concentration of hydrogen cations effect the ion release of titanium. In chloride containing solutions titanium oxide exhibits an amphoteric behaviour, which cannot be observed in fluoride containing solutions.

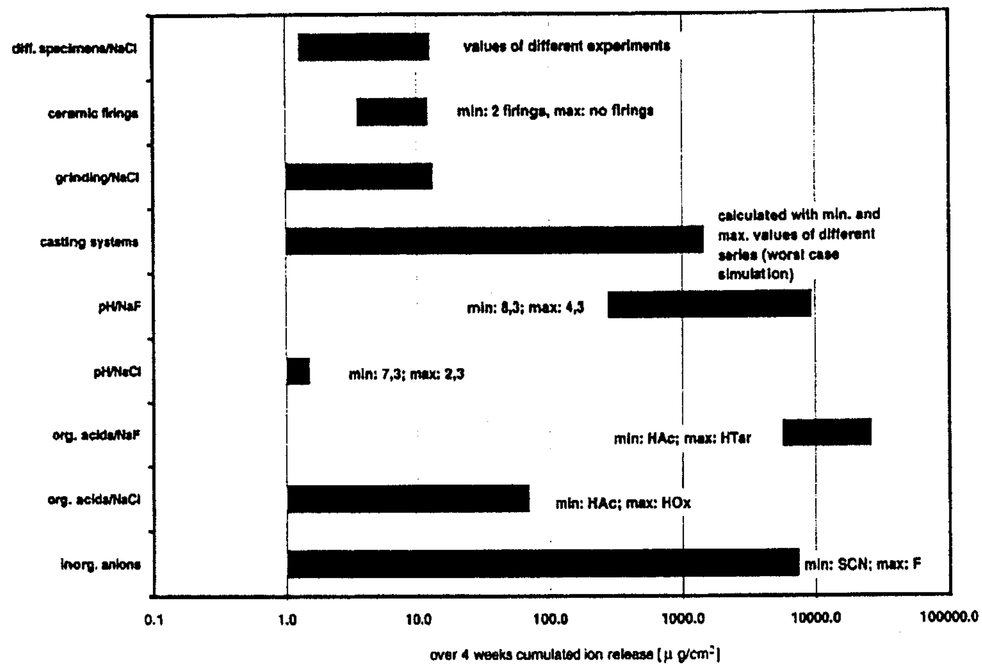

Fig. 4. Comparison of the influences of casting, simulated firings, inorganic and organic ions, pH-value and grinding on the corrosion behaviour of titanium.

In Fig. 4 different influences are compared. Simulated ceramic firings [36, 37], grinding [38], casting systems, organic anions and pH-value are influencing the ion release of titanium only little. The ion release of different test specimens under comparable conditions differ in the same order of magnitude. As discussed the ion release is accelerated by fluoride ions about 10000 times compared with chloride or thiocyanate ions. Inorganic anions exhibit the highest influence on titanium corrosion.

Although in vitro corrosion investigations are important to value the biocompatibilty of dental materials the results must be regarded very carefully. Only when compared with in vivo and clinical investigations the biocompatibility of a material can be valued. In the case of titanium in vitro, in vivo and clinical investigations reveal the same results confirming a high biocompatibility.

References

[1] Okazaki Y, Ito Y, Ito A, Taeishi T. Effects of alloying elements on corrosion resistance of titanium alloys for medical implants. In: Fujishiro S, Eylon D, Kishi T, editors. Metallurgy and technology of practical titanium alloys. The Minerals, Metals & Materials Society, 1994:313–21.

[2] Steinemann SG. Titan als werkstoff der chirurgie und zahnmedizin teil 2: korrosion und hydrolyse der reaktionsprodukte. Quintessenz 1996;48:1107–15.

[3] Steinemann SG. Titan als werkstoff der chirurgie und zahnmedizin teil 1: korrosion und gewebereaktion. Quintessenz 1996;47:971–80.

[4] Steinemann S. The properties of titanium. In: Schoeder A, Sutter F, Krekeler G, editors. Oral Implantology. New York: Thieme Medical Publishing, 1991.

[5] Bergman B, Bessing C, Ericson G, Lundqvist P, Nison H, Anderson M. A 2-year follow-up study of titanium crowns. Act Odontol Dent 1990;44:165–72.

[6] Adell R, Lekhom U, Rockler B, Branemark P-I. A 15-year study of osseointegrated implants in the treatment of the edentulous jaw. Int J Oral Surgery 1981;10:387–416.

[7] Brånemark P-Iea. Osseointegrated implants in the treatment of the edentulous jaw—experience from a 10-year period. Scand Plastic Reconstructive Surgery 1977;11:(suppl):16.

[8] Andersson M, Carlsson L, Persson M, Bergman B. Accuracy of machine milling and spark erosion with a CAD/CAM system. J Prosthet Dent 1996;76:187–93.

[9] Arango J, Stein RS, Millstein PL. Castabilitiy and marginal fit of pure titanium castings. J Dental Res 1991;70:2187.

[10] Augthun M, Schädlich-Stubenrauch J, Sahm PR. Untersuchungen zur Oberflächenbeschaffenheit von gegossenem Titan. Dtsch Zahnärztl Z 1992;47:505–7.

[11] Baez RJ, Nonaka T, Blackman R. Ti castability and surface characteristics with three phosphate bonded investments. J Dental Res 1989;70:1757.

[12] Bessing C, Bermann M. The castability of unalloyed titanium in three different casting machines. Swedish Dental J 1992;16:109–13.

[13] Brauner H. Zur Randschichtaufhärtung an titanwerkstoffen durch unterschiedliche formstoffe und einbettmassen. Deutsch Zahnärztl Z 1992;47:511–5.

[14] Herø H, Syverud M, Waarli M. Mold filling and porositiy in castings of titanium. Dent Mater 1993;9:15–8.

[15] Hopp M. Besonderheiten des Titangusses im Dentallabor. Quintessenzs Zahntech 1995;21:665–79.

[16] Klinger E, Böning K, Walther M, Titanguß—Formfüllungsvermögen und Paßgenauigkeit. Dtsch Zahnärztl Z 1991;46:743–5.

[17] Lenz E, Dietz W. Die Randschichten von Titangußobjekten unter dem Einfluß verschiedener Einbettmassen. Quintessenz Zahntech 1995;21:633–45.

[18] Lubberich AC. Das Morita-Cyclarc-System—Vakuum-Druck-Guß mit Schutzgasspülung. Dent Lab 1992;40:1063–8.

[19] Lubberich AC. Das Ohara-Titan-Dentalgußsystem— Schleuderguß unter Argon-Atmosphäre. Dent Lab 1992;40:1203–7.

[20] Lubberich AC. Die Rematitan-Gießanlage—Vakuumschmelzen im Zweikammersystem. Dent Lab 1992;40:1485–8.

[21] Lubberich AC, Mönkmeyer U. Individuelle Möglichkeiten der Titangußtechnik—Theoretische Grundlagen und konkrete Fallbeschreibung. Implantologie 1992;1:61–71.

[22] Ott D. Die Entwicklung eines Verfahrens. Das Gießen im Dentallabor. Dent Lab 1990;38:805–7.

[23] Ott D. Gießen von Titan im Dentallabor. Zahnärztl Welt 1991; 100:106–10.

[24] Päßler K, Bestelmeyer F, Ohnmacht P, Sernetz F. Einflüsse auf die Qualität und Eigenschaften von dentalen Titangüssen. Dent Lab 1991;39:809–15.

[25] Päßler K, Mann, E. Der dentale Titanguß—Grundlagen, Technologie und werkstoffkundliche Bewertung. Quintessenz Zahntech 1991;17:717–26.

[26] Päßler K. Die Weiterentwicklung des Rematitan-Systems. Quintessenz Zahntech 1995;21:649–61.

[27] Schädlich-Stubenrauch J, Augthun M, Sahm PR. Untersuchungen zu den mechanischen Eigenschaften und zur Porenbildung von Titan bei verschiedenen Gußverfahren. Dtsch Zahnärztl Z 1994;49:774–6.

[28] Stoll R, Okuno OM, Stachniss V. Titangußtechnologie—Möglichkeiten, Probleme, Hoffnungen. Zahnärztl Welt 1991;100:38–42.

[29] Takahashi J, Kimura H, Lautenschläger EP, Chern Lin JH, Moser JB, Greener EH. Casting pure titanium into commercial phosphate-bonded SiO_2 investments molds. J Dent Res 1990; 69:1800–5.

[30] West JM. Basic corrosion and oxidation. 2nd ed. London: Wiley, 1986.

[31] Cohen F, Chemla M, Burdairon G. Corrosion du titane en milieu acide fluoré: effet iatrogénique des gels topiques au fluor. J Biomat Dent 1991;7:15.

[32] Pröbster L, Lin W, Hüttemann H. Effects of fluoride prophylactic agents on titanium surfaces. Int J Oral Maxillofac Implants 1992;7:390.

[33] Siirilä HS, Könönen M. The effect of oral fluorides on the surface of commercially pure titanium. Int J Oral Maxillofacial Implants 1991;6:50–4.

[34] Strietzel R. Einfluß von fluoridhaltigen Zahnpasten auf Titanoberflächen. Zahnärztliche Welt—Zahnärztliche Rundschau—Zahnärztliche Reform 1994;103:82–5.

[35] Pearson. Hard and soft acids and basis. Stroudsburg: Dowden, Hutchinson and Rors, 1973.

[36] Kappert HF, Schwickerath H, Bregaszzi J, Veiel St, Hölsch W. Beeinträchtigung der Korrosionsfestigkeit durch den Aufbrennprozeß. Dent Lab 1995;43:65–76.

[37] Strietzel R, Görlitz P, Bochdam K-U, Borowski I. In-vitro-Korrosion von NEM-Legierungen und Titan. Dent Lab 1997;45:723–9.

[38] Hösch A, Strietzel R. Einfluß des Schleifens auf die Ionenabgabe von metallischen Werkstoffen. Dtsche Zahnärztl Z 1994;49: 698–700.