Comparison of the biocompatibility and corrosion properties of a CoCr sinter alloy with a casting alloy

CoCr sinter alloy vs.CoCr casting alloy

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Non-precious metal alloys are available in dental technology for the casting procedure, selective laser melting (SLM) and as fully dense blanks for the CAD/CAM technique. New CoCr blanks are now available which are milled in the green body state and then densely sintered. Tests must be undertaken to provide users with the assurance that this type of alloy constitutes a very good product. For this the Ceramill Sintron sinter alloy was tested in comparison with Girobond NB casting alloy with regard to their biocompatibility properties in accordance with DIN EN ISO 10993 and corrosion resistance in the immersion test in accordance with DIN EN ISO 10271/22674. The results of the tests are documented in the following article.

Introduction

All dental restoration materials fitted in the oral cavity are subject to the Medical Devices Directive for approval as a medical product. The standards and guidelines of the Medical Devices Directive regulate the requirements to be fulfilled to ensure safety for the user and in particular for the patient. Two essential requirements with alloys are the biocompatibility and corrosion behaviour.

The biocompatibility or also tissue compatibility of dental materials has developed into a comprehensive, complex and independent branch of materials science [1]. A material is biocompatible if the material behaves inert* in its prescribed application or the substance release is low or acceptable, i.e. not a sufficient amount to damage the organism of the patient. Corrosion tests provide important information about the release of substances. Intolerability reactions always imply corrosion processes, which then as metal protein compounds or metal-cell complex compounds can cause biological damage [2]. Adequate corrosion stability therefore provides the basis for good biocompatibility. To ensure good biocompatibility it is important that there are no cytotoxic effects or any negative effects etc. for the organism when using dental materials. Allergological aspects should also be taken into consideration in biological testing.

Only once all the requirements of tissue compatibility have been fulfilled, i.e. it is proven that a new material does not have any negative effects for the patient during its use, can approval be given in the respective Class in accordance with the Medical Devices Directive.

Fig. 1a Dental restorations ...

Literature

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The literature list can be obtained using the QR code above or at www.teamwork-media.de. Follow the link “Literaturverzeichnis“ in the eft sidebar.

* Chemically inert (Latin for non-involved, sluggish) describes substances which under the respective conditions do not react or react negligibly with potential reaction partners.

Fig. 1b ... fabricated using Ceramill Sintron CoCr sinter alloy

With CAD/CAM materials the term biocompatibility is mainly used in association with zirconia. Non-precious metal (NPM) alloys can also have very good properties in this context. The following documented tests are intended to demonstrate whether this applies for the new Ceramill Sintron CoCr sinter alloy available to the dental market.

Description

In this article the biocompatibility and corrosion properties of Ceramill Sintron will be more closely examined as a medical product and compared with a conventionally fabricated, precision dental casting (Girobond NB) (Table 1).

Both products are manufactured and sold by Amann Girrbach. They are used for the fabrication of fully anatomical and anatomically reduced crown and bridge restorations (Fig. 1a and 1b).

Metals in the form of alloys (mixtures of different metals) have been used and fitted successfully for many years in the fabrication of restorations with very different applications (crown and bridge technique, partial prosthetics, fillings, implant technique).
By far the most important requirements of alloys, which are used in dentistry, are exceptionally high biocompatibility and corrosion resistance. Metal alloys used for dental purposes are subjected in the oral cavity to extremely high loading, which influences these requirements. This includes, e.g. permanently moist conditions, fluctuations in temperature and pH and mechanical stresses due to mastication or bruxism. Due to these

Tab. 1 – Chemical composition in % by weight according to the manufacturer's specifications

Elements	Ceramill Sintron	Girobond nb
Cobalt (Co)	66	62
Chrome (Cr)	28	26
Molybdenum (Mo)	5	5
Tungsten (W)	–	5
Silicon (Si)	–	1,2
Cerium (Ce)	–	0,3
Other elements (Mn, Si, Fe)	<1	–
Other elements (Nb, Fe, N)	–	<1
According to DIN EN ISO 22674:2007 free of ...	... nickel, beryllium, gallium and cadmium	... nickel, beryllium, gallium and carbon

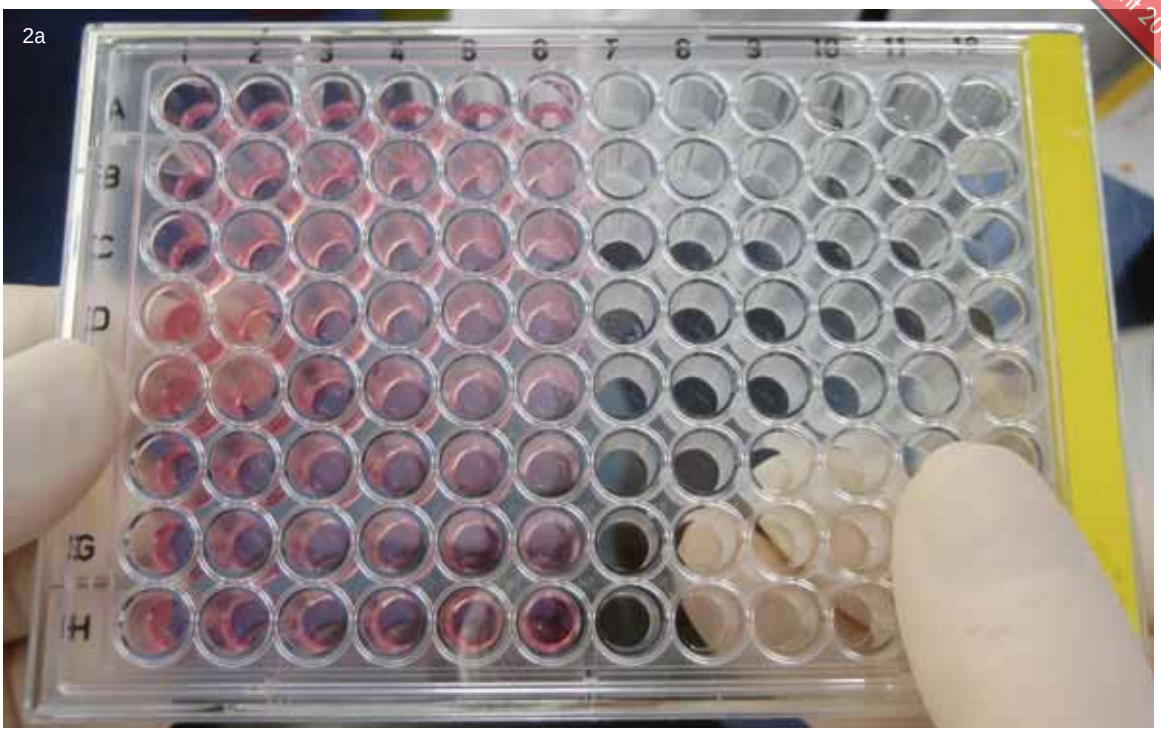

Fig. 2a
The cytotoxicity is ascertained in cell culture tests. …

stresses it is virtually unavoidable that components are released from the metal restoration into the oral cavity, which is known as corrosion. Consequently corrosion products released from dental alloys can cause undesired side effects, such as local toxic, systemic toxic or allergic reactions in the immediate proximity of the dental restoration or in other areas in the human organism. Research, investigation and testing of the biological properties of dental materials, including the above-named side effects, are combined under the term biocompatibility. The biocompatibility test is primarily intended to ensure not only the safety of the patient but also that of dentists, dental practice personnel and dental technicians. The explanations up until now and the fact that the compatibility of a material is determined by the release of substances from the material (solubility, corrosion) indicate that the terms biocompatibility and corrosion stability are intrinsically linked with one another.

The first section of the article deals with the subject of the biocompatibility tests of Ceramill Sintron. The main section is formed by the tests on the corrosion properties of Ceramill Sintron in comparison with Girobond NB casting alloy, which were conducted by the Section of Medical Materials and Technology (IMT) at the Centre of Dentistry, Oral Medicine and Maxillofacial Surgery of the University of Tübingen.

Part 1: Testing the biocompatibility of Ceramill Sintron

The spectrum of biological hazards is a comprehensive and extensive subject area because of the abundance of existing and offered medical products nowadays. The DIN EN ISO 10993 series is an extensive set of rules that contributes to the protection of humans against possible biological risks when using medical products. It describes a variety of tests which may be necessary for assessing the biological safety of a medical product for use on patients [3].
For approval of Ceramill Sintron as a medical device the following biocompatibility tests were completed in accordance with DIN EN ISO 10993 by an accredited test laboratory, BIOSERV Analytics and Medical Devices Ltd, Rostock, Germany:

- Cell damage (cytotoxicity)
- Hypersensitivity (allergy test, sensitisation)
- Local toxic reactions (intracutaneous reactivity)
- Systemic toxic reactions (acute systemic toxicity)

The toxicity of substances, i.e. their potential to cause damage to the organism chemically, is assessed in the cytotoxicity test. Any possible damaging effects of medical products on individual cells (for example cell necrosis, cell proliferation) are investigated in the cell culture test (isolated cells from human or animal tissue). The grade of toxicity is given as a measure of the cell damage, which can range from that of intact cell cultures (Grade 0) to destroyed cell cultures of more than 75 % (Grade 4). Cell culture tests are easy to perform and reproduce and are therefore ideal for initial evaluation of the biocompatibility (Fig. 2a and 2b). However, the overall transferability of the results of cell culture tests to the living organism is debatable [4].

To intensify the test conditions slightly a test was performed with an extended test duration of 72 hours in addition to the standard cytotoxicity test of 24 hours.

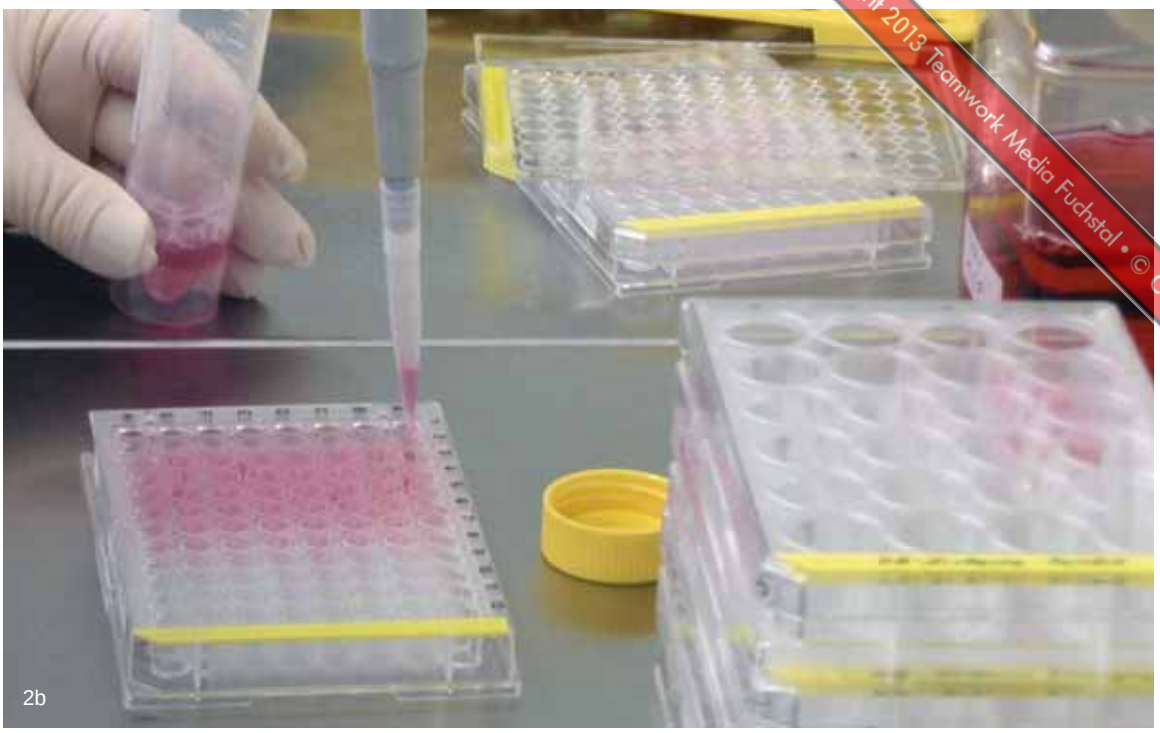

Fig. 2b
… these are easy to perform and reproduce and are therefore ideal for evaluation of the biocompatibility

In the allergy test the hypersensitivity (allergic reaction) of the organism was tested, which was triggered by a medical product in the animal experiment. The degree of allergenicity, which can range from weak (Grade 1) to extreme (Grade V), was derived from the results over a test duration of 24 and 48 hours. Local toxic reactions include non-allergic reactions in immediately adjacent tissue or contact areas to the medical product (e.g. irritation of the oral mucosa). The test for intracutaneous reactivity in the animal experiment over 24, 48 and 72 hours is used to assess local tissue reactions caused by medical products. Local toxic reactions can be graded from no discernible reactions (Grade 0) to severe reactions (Grade 4).

Damage of organs or impairment of their functions in indirect proximity to medical products is described as systemic toxic reactions. Such damage could be caused by released substances in the oral cavity, which could enter the organism by swallowing with the saliva or via the bloodstream. The degree of the reaction, which can range from normal (Grade 0) to death of the test animals (Grade 4), is assessed in the animal experiment over 4, 24, 48 and 72 hours.

Results of the biocompatibility of Ceramill Sintron

The results and their significance and assessment for the four biocompatibility tests performed on Ceramill Sintron are listed in Table 2.

Tab. 2 – Results of the biocompatibility tests of Ceramill Sintron

Test	Cytotoxicity	Allergenicity (sensitisation)	Intracutaneous reactivity (irritation)	Acute systemic toxicity
Test duration	24 h + additional 72 h	24 h, 48 h	24 h, 48 h, 72 h	4 h, 24 h, 48 h, 72 h
Result	Cytotoxicity Grade: 0	Allergenicity Grade: 0	Irritation Grade: 0.0	Reaction Grade: 0
Significance	0 = no cell damage	0 - 8 = weak (Grade I)	0.0 - 0.4 = negligible	0 = normal (no symptoms)
Assessment	[…] the material tested did not cause any toxicologically/biologically critical cell damage […]	[…] no allergenic substances could be derived from the material tested […]	[…] the material tested did not cause any intracutaneous reactions […]	[…] the material tested did not cause any toxicological reactions […]

The test results indicate that Ceramill Sintron fulfils the biocompatibility requirements according to the DIN EN ISO 10993 Standard and is classified as tissue compatible with the prescribed specific application. There was also absolutely no cell damage established during the cytotoxicity test with extended test duration over 72 h.
According to the applied standard the allergenic risk is rated with lowest possible category.
In comparison with Girobond NB casting alloy, which has been clinically proven and successfully used for many years, both alloys are rated equally in terms of the biocompatibility properties established in this study.

Part 2: Testing the corrosion properties

The static immersion test, which is the standard procedure for assessing the corrosion properties of dental alloys, was used in the present study for testing the corrosion properties. The loss of mass is also determined in the immersion test by examining the solubility of a metal test piece under simulated oral cavity conditions. In the test a metal test piece is immersed in a solution of artificial saliva and remains in the solution for a specific period of time. To measure the solubility of the test pieces the amount of metal ions released is determined as the mass loss per test piece surface (µg/cm²) in the given period of time. According to the Standard DIN EN ISO 22674 the loss of mass of dental materials should not exceed the value of 200 µg/cm² in 7 days.

Material and method
The geometry of the test piece for the static immersion test is shown in Figure 3. Twelve plates were each fabricated from Girobond NB and Ceramill Sintron for the corrosion tests.
The Standards DIN EN ISO 22674 [4] and DIN EN ISO 10271 [5] were used as a basis.
Figures 4a to 4c show the fabrication of the plate test pieces using the example of Girobond NB. The plates were milled from a wax blank (Ceramill WAX) (Fig. 4b) based on a CAD dataset (Fig. 4a) using the Ceramill Motion 1. The test pieces were then sprued using 3 mm and 5 mm wax wires (Fig. 4c) and invested and preheated according to the manufacturer's instruction in the speed technique using Giroinvest Super (Amann Girrbach). The moulds were cast using the Heracast IQ (Heraeus) vacuum pressure casting machine. After devesting and trimming of the sprues, the surfaces of the plates were prepared on the Phoenix Beta (Buehler) grinding and polishing machine using silicon carbide sandpaper, grit size 1 200 under water cooling (Fig. 4d). The Ceramill Sintron plates were directly milled from CoCr blanks using the same dataset and sintered (Fig. 4e and 4f) as described on Page 25. The surfaces were prepared in the same way as the cast test pieces.
According to the present standards the alloys, which according to the manufacturer are also suitable for porcelain veneering, should also be tested in the heat treated state. This is intended to assess whether bonding alloys also maintain their properties after the effects of heat - as is the case with porcelain veneering - compared with the untreated state. For this reason the sequence of a porcelain veneer was simulated on half of each of the fabricated test pieces per alloy according to the firing specifications for the conventional veneering porcelain Creation CC (Creation Willi Geller) (Fig. 5a and 5b).

A firing sequence of one oxide firing and four firing cycles is required in DIN EN ISO 22674. DIN EN ISO 10271 recommends heat treatment for 10 min at the highest firing temperature according the

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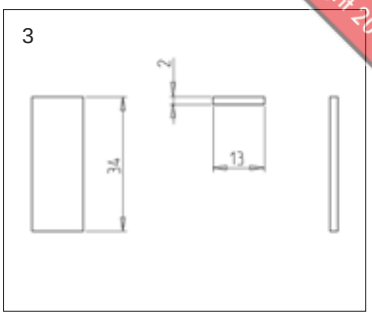
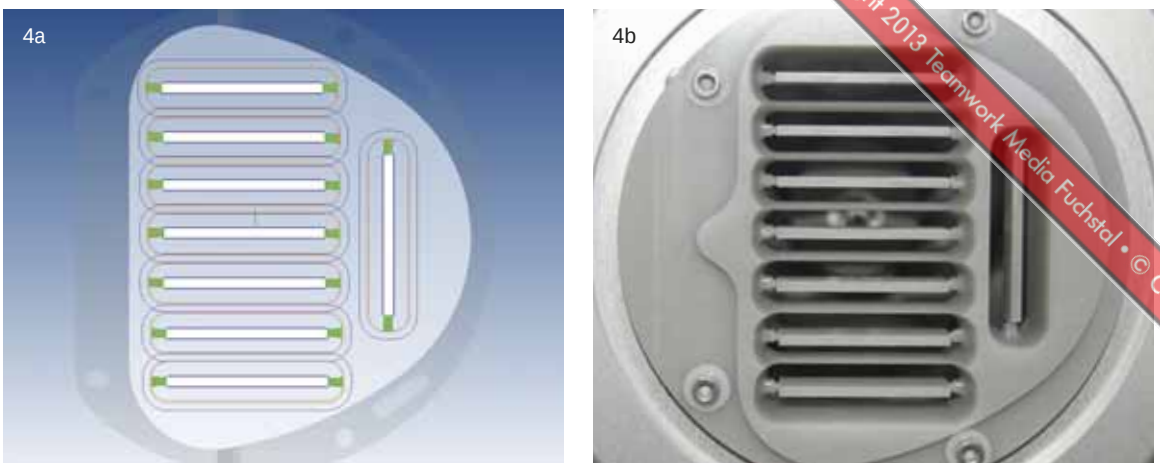


Fig. 3 Design drawings of the test pieces for the static immersion test for examining the corrosion properties

Tab. 3 – Firing chart for heat treating the test pieces

Firing	Start temperature	Close time	Temperature rate	Vacuum	Final temperature	Hold time
Oxide firing	550 °C	–	80 °C/min.	–	1000 °C	1 min.
1st Opaque	550 °C	6 min.	80 °C/min.	+	1000 °C	1 min.
2nd Opaque	550 °C	6 min.	80 °C/min.	+	950 °C	1 min.
1st Dentine	580 °C	6 min.	55 °C/min.	+	920 °C	1 min.
2nd Dentine	580 °C	4 min.	55 °C/min.	+	910 °C	1 min.
Glaze firing	600 °C	2 min.	55 °C/min.	–	930 °C	–



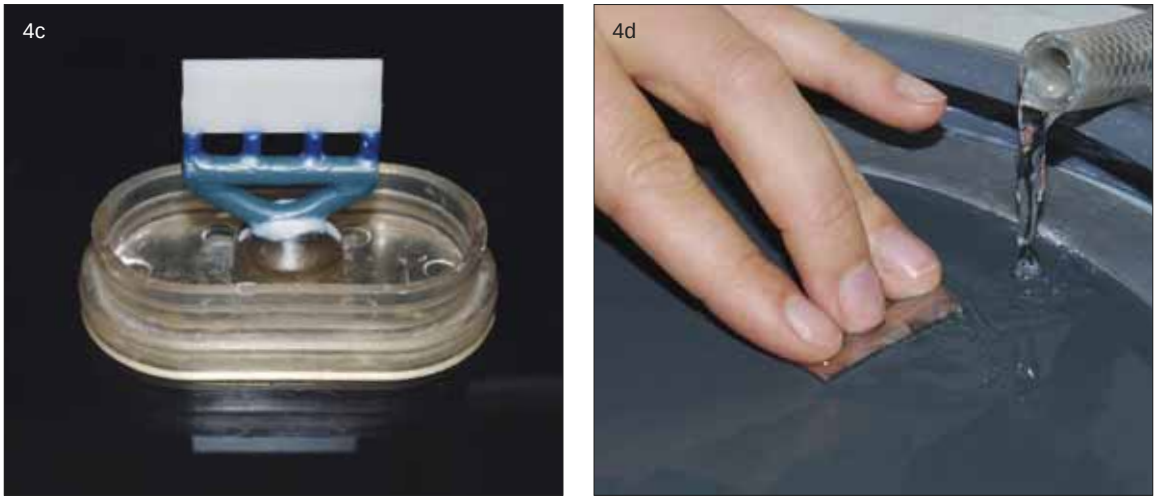


Fig. 4a to 4d Fabrication of the test pieces for the statistical immersion test using the example of Girobond NB CoCr casting alloy: milling in wax; spruing, investing and casting; trimming the test pieces

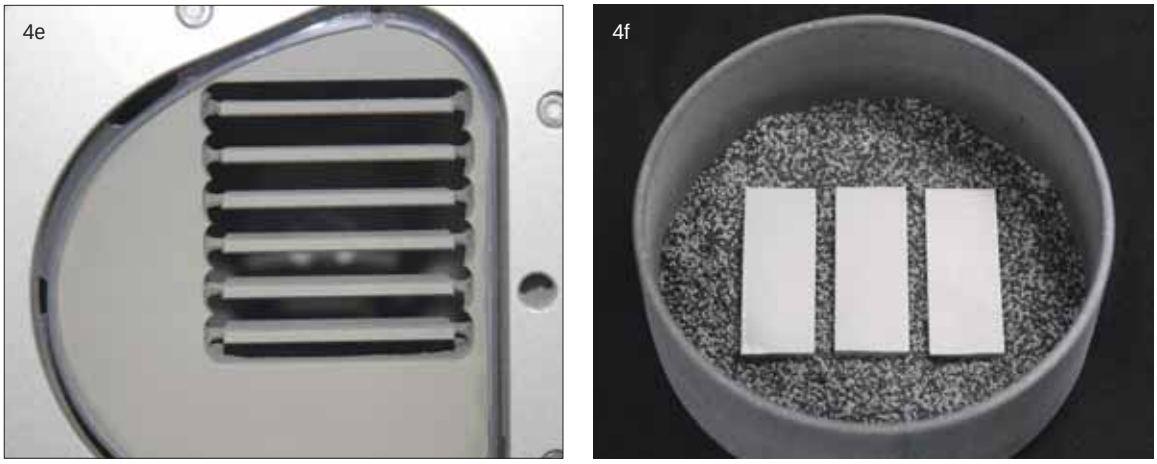


Fig. 4e and 4f The Ceramill Sintron test pieces were based on the same CAD dataset as the Girobond NB test pieces. However, after milling the test pieces were separated from the blank and densely sintered

alloy manufacturer. To intensify the test condition six test pieces of each alloy were subjected to three porcelain firing sequences each with six firing cycle in a conventional porcelain furnace (Table 3). The plates were heat treated before surface preparation with 1200 silicone carbide sandpaper.

Corrosion measurements (immersion test)

The corrosion properties were tested and determined using the static immersion test according to DIN EN ISO 10271 by the Department of Medical Materials and Technology at the Centre of Dentistry, Oral Medicine and Maxillofacial Surgery at the University Hospital, Tübingen. The electrolyte (artificial saliva) for the immersion test consisted of 0.1 mol/L lactic acid and 0.1 mol/L NaCl (pH 2.3). The immersion test was performed in 15 ml plastic tubes (PP) with caps.

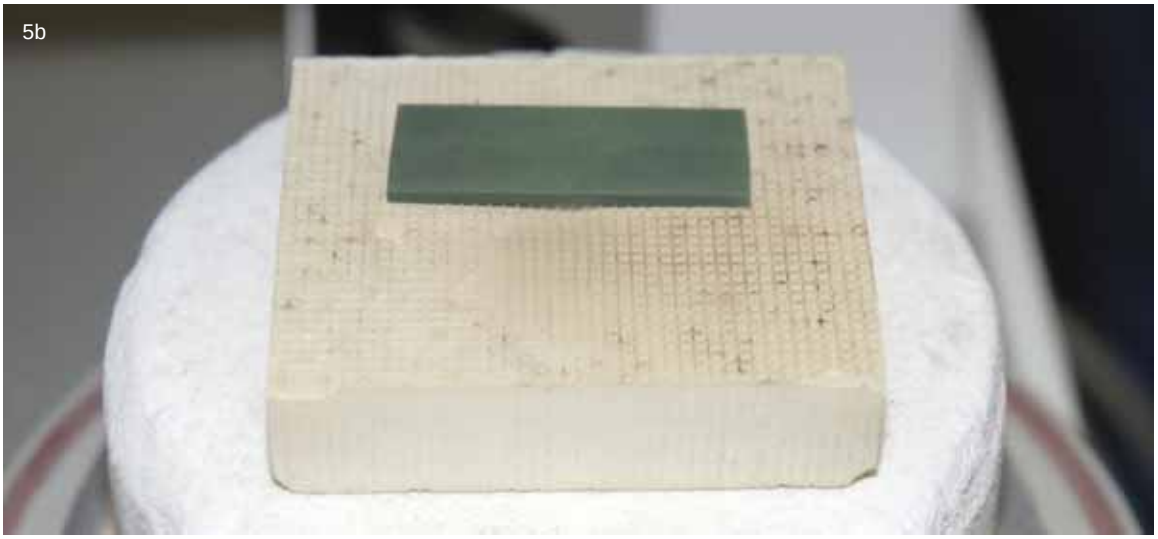


Fig. 5a and 5b According to the present standards alloys, which are also suitable for bonding porcelains, should also be tested in the heat-treated state

The test pieces were cleaned with ethanol in an ultrasonic cleaner for 3–5 min. before placing each individual test piece in one of the plastic tubes. Care was taken to ensure that there was minimal contact of the test pieces with the tubes. Then 10 ml of test solution was filled into the tubes and the tubes were sealed to prevent evaporation of the solution (Fig. 6). The test pieces/tubes were heated in an incubator to 37±1 °C. The test period for the immersion test was seven days. The electrolyte was changed after one day and four days and the test pieces were removed from the tubes after seven days. The elements that had been immersed in the solution were analysed using an Optima 4300 DV ICP-OES spectrometer (Perkin-Elmer) (Fig. 7a und 7b). Standard solutions were prepared for calibration using the test solution.

Every element immersed in the solution was determined at two different wavelengths and three sequential measurement cycles using the spectrometer. The means were calculated from the measurements.

The detection sensitivity of the concentrations of the tested alloy elements was ascertained as <0.03 mg/L (blank detection limit). The amount of eluted elements was converted to µg/cm².

Results of the corrosion test

Figure 8 and 9 show the averaged mass loss from six test pieces of each alloy with and without heat treatment (Table 4a and 4b).

The results indicate that the Co release of the two alloys is very low with values below 1 µg/cm² and is even lower with the heat treated test pieces. The only differences with regard to this are in the time period of the Co release. With Ceramill Sintron there was a decrease of 0.52 on the first day to 0.06 µg/cm² on the seventh day (no heat treatment).

Tab. 4a – Analytically (ICP-OES) determined mean loss of mass (n=6)

Day	Heat treatment	Mo	Co	Ce	Cr	Fe	Nb	Si	W
Ceramill Sintron									
1	without	0,00	0,52	–	0,09	0,00	–	0,31	
	with	0,00	0,38	–	0,07	0,00	–	0,30	–
4	without	0,00	0,12	–	0,00	0,00	–	0,30	–
	with	0,00	0,10	–	0,00	0,00	–	0,30	–
7	without	0,00	0,06	–	0,00	0,00	–	0,31	–
	with	0,00	0,05	–	0,00	0,00	–	0,30	–
Girobond NB									
1	without	0,00	0,52	13,80	0,03	0,00	0,07	0,37	0,00
	with	0,00	0,38	10,65	0,03	0,00	0,07	0,34	0,00
4	without	0,00	0,12	25,38	0,03	0,00	0,13	0,72	0,00
	with	0,00	0,10	19,90	0,03	0,00	0,15	0,68	0,01
7	without	0,00	0,06	31,95	0,03	0,00	0,20	1,05	0,00
	with	0,00	0,05	25,11	0,03	0,00	0,22	1,00	0,01

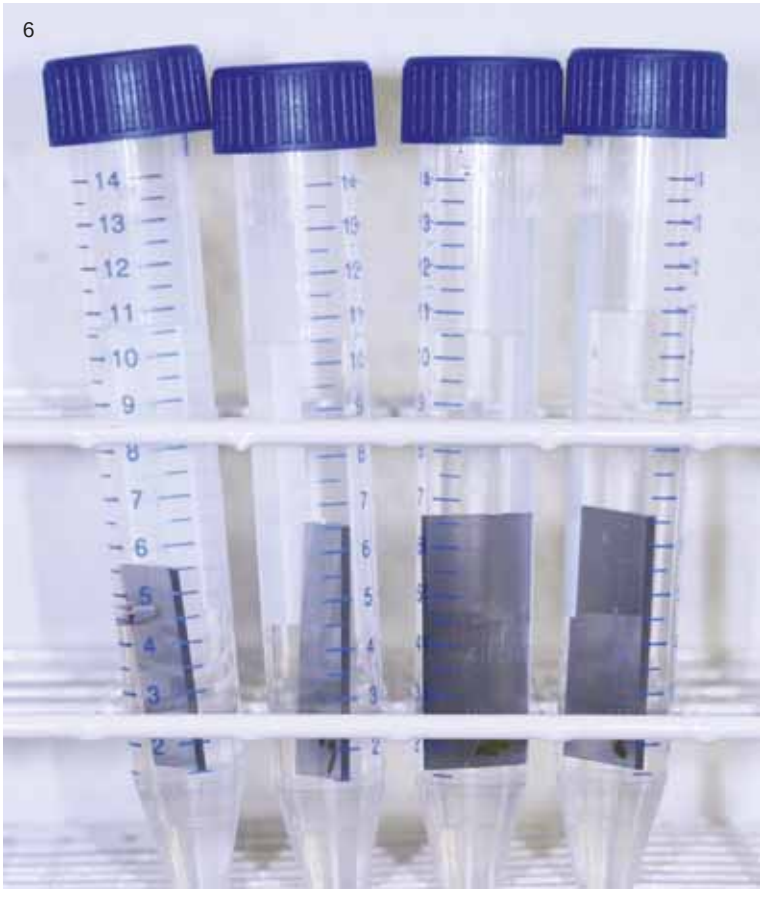


Fig. 6
The test pieces are immersed in 10 ml artificial saliva for testing and determining the corrosion properties

The values reduced from 0.38 (day one) to 0.05 µg/cm² (day seven) with heat treatment. With Girobond NB there was virtually no change in Co release over seven days of immersion testing without heat treatment; in contrast there was an increase in Co release after heat treatment. There was a similar behaviour with the element Si, which remained unchanged with Ceramill Sintron in both states at 0.3 µg/cm². In the case of Girobond NB the mass loss increased in both states from 0.3 to 1 µg/cm². With Girobond NB the high solubility of the element cerium is notable, which mainly goes into solution and its loss of mass increases over the course of seven days. This is the case both with and without heat treatment. The high mass loss of cerium is the reason for the differences in the accumulated total loss of mass.

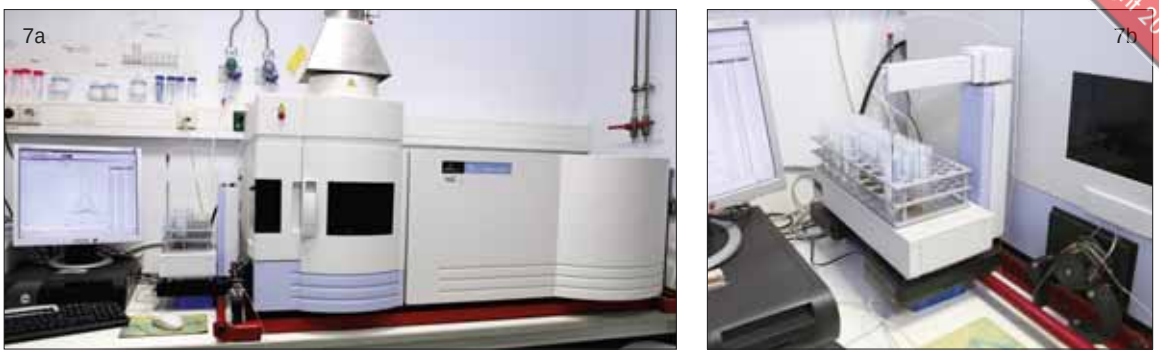


Fig. 7a and 7b ICP spectrometer used for analysis of the metal ions released into the solution and determination of the loss of mass

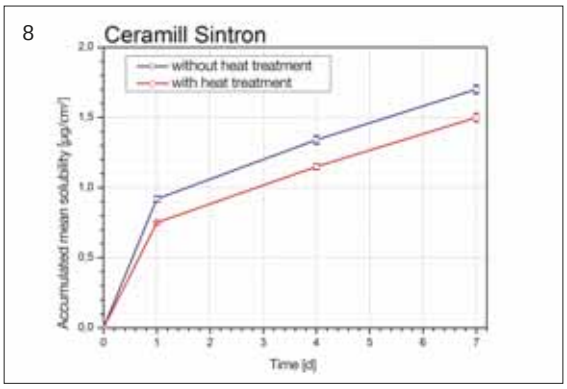


Fig. 8 Accumulated mean loss of mass of Ceramill Sintron over seven days of immersion in artificial saliva

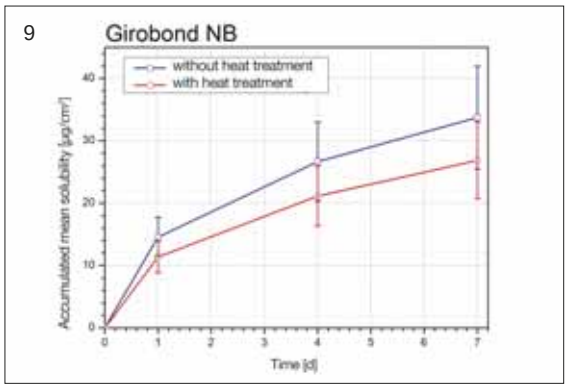


Fig. 9 Accumulated mean loss of mass of Girobond NB over seven days of immersion in artificial saliva

Conclusion

The two alloys fulfil the requirements of ISO 22674 and are well below the maximum threshold limit value of 200 µg/cm² required by the Standard (in the opinion of the authors set much too high). The chemical solubility of Girobond NB is also very low with regard to the main components (Co, Cr, Mo). The element cerium (element symbol Ce) has the highest value with the casting alloy. Similar to the casting and sinter alloys tested in this study, a low Co release was also established with CoCr alloys which were processed using the SLM technique. The corrosion behaviour of the sinter alloy therefore integrates in the existing range of CoCr alloys that can be processed.

Overall the chemical solubility of Ceramill Sintron is very low. This is due to the good biocompatibility results that were also ascertained.

Tab. 4b – Mean overall mass loss of all elements

Day	Total [µg/cm²]			
	Ceramill Sintron		Girobond NB	
	nHT*	wHT**	nHT*	wHT**
1	0,92	0,75	14,58	11,38
4	1,34	1,15	26,68	21,16
7	1,70	1,50	33,73	26,86

About the authors

The CV of the authors can be found at www.teamwork-media.de/download/authors/dd1_13_sintron2.pdf or directly using the adjacent QR code.

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* nHT = no Heat Treatment/ ** wHT = with Heat Treatment