dental dialogue

The International Journal of Dental Technology

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Millable CoCr blanks for in-house manufacture: value creation, control and convenience

CoCr-Revolution

An article by Dipl.-Ing. Falko Noack, Dornbirn/Austria

For a long time CAD/CAM was equated with zirconia. The reason was that in-house manufacture only experienced a boom with the introduction of pre-sintered zirconia. The health reforms and also the reduction in real wages ensured that there was an increase in the demand for non-precious metal alloy restorations. CAD/CAM-supported manufacture is suitable for fabricating non-precious restorations. However, very high demands are placed on the manufacturing unit (coolant delivery, rigidity of the machine etc.), which is why this class of material often had to be ordered from centralised manufacture/manufacturing centres. Amann Girrbach provides the ideal opportunity of fully utilising a CAD/CAM system in-house in the laboratory with Ceramill Sintron CoCr blanks, which can be dry milled in-house and are therefore a very attractive option.

Product idea

Further development in the CAD/CAM sector primarily involved an increasing demand for additional materials. Though ceramic materials and plastics are now readily available for CAD/CAM in-house manufacture, a gap still exists in the application of one of the most successful and widespread classes of dental restoration materials. I refer to NPM* alloys. Special CoCr alloys make up a large proportion of dental restoration materials. Up until now, however, this type of material could only be processed with the support of CAD/CAM in centralised manufacture (laser-melting process) or on large, cost-intensive milling machines (milling from the dense material). The aim of developing Ceramill Sintron was therefore to close this gap and develop a millable blank, including the manufacturing process, which enables cost-effective processing of CoCr in the CAD/CAM in-house sector. The basic product requirements were defined as follows:

- Milling properties similar to pre-sintered zirconia
- Direct processing of the material without additional casting procedure
- Time-efficient sintering of the material
- Compliance with all material properties relevant in dental technology
- Veneerability of the material using commercially available bonding porcelains
- Cost-effective manufacturing process for CoCr frameworks

Product description

Ceramill Sintron blanks are in the green body state and comprise a CoCrMo alloy held together by an organic binder. The alloy is used for the fabrication of fully anatomical and anatomically reduced crown and bridge frameworks and is suitable for the fabrication of fixed or removable restorations using CAD/CAM systems (Fig. 1) in accordance with DIN EN ISO 22674. Restorations fabricated using this material are fitted in the oral cavity of patients as invasive products for long-term use. It is therefore a Class IIa medical device.

The material is processed in a wax-like state (unsintered metal powder held together by a binder = green body) and then sintered in a high-temperature sinter furnace developed specifically for this material. This sintering process is completed under an argon shielding atmosphere (Argon 4.6) using a preset temperature programme tailored to the alloy and this process reduces the dental framework to its pre-calculated final size. In the sintered state the material has the properties required for a Type 4 alloy (DIN EN ISO 22674), which is comparable with CoCrMo casting alloys that have been used successfully for many years. Further processing/conditioning in the dental laboratory, such as bonding a porcelain veneer or repairing by laser welding, is also possible and comparable with CoCrMo casting alloys. It has therefore been possible to develop a material that combines the properties of two successful and clinically proven materials.

Indices

- CAD/CAM
- CoCr alloy
- Milling process
- Green body
- In-house manufacture
- Sintering

* NPM or non-precious metal alloys are generally chrome-cobalt alloys

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Fig. 1 Ceramill Sintron blanks comprise a CoCrMo alloy in the green body state and are used for CAD/CAM-supported fabrication of fully anatomical and anatomically reduced crown and bridge frameworks

Mechanical, physical properties after final sintering

Tensile strength (Rm)	830 MPa
0.2 % Proof stress (Rp0,2)	450 MPa
Modulus of elasticity (E)	200 GPa
Elongation at rupture	20 %
Vickers hardness (HV 10)	280
Coefficient of thermal expansion (25-500 °C)	14,5 *10-6/K

Working stages for fabricating a CoCrMo framework

A. Casting procedure	B. CAD/CAM-Sinter process
1. Model fabrication, articulation	1. Model fabrication, articulation
2. Model preparation (hardening, die spacer application)	2. Model scan
3. Wax-up	3. CAD design
4. Spruing	4. CAM (milling of the framework from a CoCrMo blank)
5. Investing	5. Separating and trimming
6. Preheating and casting	6. Sintering
7. Devesting and sandblasting	7. Polishing or preparing for porcelain firing
8. Cutting off the sprues	
9. Trimming	
10. Polishing or preparing for porcelain firing	

The chemical composition, macroscopic appearance, mechanical and biological properties and processing characteristics in the sintered state are identical in practical terms to those of CoCrMo casting alloys that have been clinically proven for many years.

Processing of raw components in a preliminary material stage using CAD/CAM technology and then sintering the zirconia, which is also used as a ceramic framework material for dental restorations, have been familiar processes for some years and are now state-of-the-art technology. As well as having a large number of features in common with casting alloys, Ceramill Sintron also has the following advantages:

- No or only minimal traces of oxidation due to the sinter process under shielding gas
- Use of the material in a highly automated CAD/CAM process ensures increased process reliability
- Improved reproducibility of the final results, as the possibilities of manipulation have been reduced compared with the casting procedure
- Homogeneous and identical alloy composition in the entire reconstruction, as melting of the alloy is no longer required
- No obvious disadvantage compared with casting in terms of material consumption (sprues of cast restorations should also not be reused)
- Time-saving in the fabrication of dental restorations (fewer working stages for the dental technician)
- Lower material costs, as consumable materials required for waxing up and casting (investment, wax etc.) are not required

Manufacturing process

The table contains a list of comparisons (see above) of the process stages for fabricating a CoCrMo framework in the dental laboratory according to the casting procedure and CAD/CAM sinter process. It is clear from the comparison that fewer working stages are required for fabricating a framework in the dental laboratory using the CAD/CAM sinter process.

Technically, the procedure with the Ceramill Sintron manufacturing process has much fewer sources of error than that of the conventional casting procedure. With Ceramill Sintron the material properties, in particular the alloy composition, remain unchanged both during the milling process and subsequent sinter process (solid-phase sintering under shielding gas atmosphere). This is not always guaranteed when casting this type of CoCrMo framework. As a result of complete melting of the alloy during the casting procedure, segregation phenomena may occur in the molten metal due to the concentration gradients. Not all alloy components are uniformly and homogeneously arranged in the structure during the solidification process. Certain areas of the structure then become impoverished while other areas are enriched with alloy components. In addition, excessively high melting temperatures may cause a reduction of the low-fusing alloy components. This alters the composition of the alloy. Also, contamination may be caused by compo-

Fig. 2 Ceramill Sintron is indicated, for example for anatomically reduced crowns and bridge frameworks in the anterior and posterior region

nents of the casting mould investment entering the alloy as a result of interactions between the molten metal and investment. It should also be noted that the casting procedure, particularly when casting using an open flame, involves heavy oxidation of the casting. This oxidation layer is removed by sandblasting after devesting of the casting. Sandblasting is an erosive, material-reducing procedure which can negatively affect the accuracy of fit, particularly in the region of the crown margin. Inexact regulation of the investment expansion can cause deformation and other inaccuracies in the fit of the casting. The alloy may also become contaminated due to residual material from the pattern (wax or resin), which can also involve changes in the alloy composition and possibly a change in the mechanical and biological properties.

All of the above risks are avoided by using the Ceramill Sintron manufacturing process. Segregation phenomena are either not possible or only to a very limited degree during the sinter process, as sintering involves diffusion-controlled material transport without the creation of a liquid phase. This is also referred to as solid-phase sintering in this context, as is known from pre-sintered zirconia. Contamination of the alloy from external sources, for example by the investment or residual waxing up materials, is excluded, as neither material is used during the manufacturing process of Ceramill Sintron. Deformation due to thermally induced stresses during the milling process is also excluded, as there are no thermal effects during the milling process of the green body. Surface oxidation is also reduced to a minimum, as sintering is completed under a shielding gas atmosphere. The sandblasting process, which is time-consuming and reduces the accuracy of fit to a certain extent, is therefore no longer required.

For the reasons described above it can be concluded that a sintering process combined with CAD/CAM milling procedures, as is used for Ceramill Sintron, has distinct advantages compared with the conventional casting procedure with regard to process reliability and reproducibility. The manufacturing process is shown in the illustrated sequence (see right).

Fig. 3 Bridge frameworks with a maximum of two connected pontics are approved in the anterior and posterior region

Ceramill Sintron Workflow

Scanning

CAD

CAM

Sintering

Further processing

Indications

Ceramill Sintron is indicated for the following types of restoration:

- Anatomically reduced crown and bridge frameworks in the anterior and posterior region (Fig. 2)
- Fully anatomical crowns and bridge restorations in the posterior region and anatomically partially reduced anterior restorations
- Bridge frameworks with a maximum of two connected pontics in the anterior region and a maximum of two connected pontics in the posterior region (Fig. 3) and a maximum anatomical length of 50 mm
- Cantilever bridges with a maximum of one pontic (one cantilever unit up to maximum the second premolar)
- Primary telescope crowns

Conclusion

The dry millable Ceramill Sintron CoCr blanks from Amann Girrbach closes the gap that up to now existed between the consequent (full) utilisation of the CAD/CAM technique and central manufacture of CoCr units. The material and accompanying procedure guarantee the user a wide range of indications and alloy characteristics, which comply with the requirements of a Type 4 alloy (DIN EN ISO 22674).
In addition, the advantages provided by CAD/CAM manufacturing can be utilised, whereby the value creation with CoCr restorations can now remain in the owner's laboratory.

Product list

Product	Name	Manufacturer
CAD/CAM software	Ceramill Mind & Match software	Amann Girrbach
CoCr blanks	Ceramill Sintron blanks	Amann Girrbach
Manufacturing unit	Ceramill Motion and/ or Ceramill Motion 2	Amann Girrbach
High-temperature sintering furnace	Ceramill Argotherm	Amann Girrbach
Sinter accessories	Ceramill Argotherm sinter box	Amann Girrbach

About the author

After about eight years working in the dental technology sector (Dental Laboratory Glaser; Boblitz/Brandenburg, Germany), during which he mainly specialised in the fixed/removable technique and implant prosthetics, Falko Noack decided to study at the University of Applied Sciences Osnabrück. After four years at the university he gained the title Dipl.-Ing in Dental Technology. During his study time he worked at the university on various projects in the field of metallography and material testing of dental materials. The topic of his diploma thesis was the development of a process chain for a zirconia pre-sintered blank manufacture. He then applied his practical and technological knowledge in research and development at Amann Girrbach, especially in the field of zirconia production and application technology. Falko Noack is now head of the Research and Development Department at Amann Girrbach.

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New technique for dry milling chrome-cobalt-molybdenum in the laboratory

Quickly milled, reliably veneered

An article by Dipl.-Ing. Bogna Stawarczyk, MSc, Marlies Eichberger, Josef Schweiger, PD Dr. Florian Beuer, all Munich, Germany, Dipl.-Ing. Falko Noack and MSc Rita Hoffmann, both Dornbirn/Austria

Thinking about dental chrome-cobalt-molybdenum alloys makes one either very hot or cold. Hot because thoughts must turn to the almost archaic casting technique with all its pitfalls and cold because fabrication of frameworks using alternative techniques must be outsourced. The required framework can of course also be fabricated using the milling technique but unfortunately the majority of laboratory CAD/CAM systems are not capable of milling the frameworks. This could change with a new chrome-cobalt-molybdenum milling blank which can be dry milled in the presintered state. A good reason to take a closer look at this material.

The rapid development of restorations fabricated with the aid of computers has been revolutionising the dental practice and dental laboratory for several years now. Tooth-coloured materials are mainly associated with the computer-aided design (CAD)/computer-aided manufacturing (CAM) technique today, however, not only ceramics and high-performance polymers but also alloys can be processed using these techniques.

In the past chrome-cobalt-molybdenum powder alloys were processed additively in manufacturing centres using the laser melting technique or processed from fully hard material using the subtractive technique on large, cost-intensive milling machines. Only a few CAD/CAM systems suitable for use in conventional dental laboratories were or are designed for processing these materials and are associated with high acquisition and maintenance costs.

New approach to processing

A new chrome-cobalt material (Ceramill Sintron, Amann Girrbach) in combination with a new processing strategy now enables this alloy to be milled in the presintered state quickly and cost-effectively using the subtractive technique. Like the most widely established processing strategy for dental zirconia, the blanks also consist of a material in a preliminary state technically. With zirconia it involves so-called “partially sintered” blanks, while the new CoCr blanks are supplied in the “green body” state. Green bodies are when the blank has not yet been debindered (compared with a partially sintered blank). This means that the powder particles are held together by an organic binder during further processing. The blank is sintered at approx. 1300 °C in a high-temperature furnace under a shielding gas atmosphere only after subtractive processing of the green body. During the sinter process the organic binders burn out and the metallic powder particles sinter together, without producing a molten liquid phase. This reduces the restoration to the pre-calculated final size (volumetric shrinkage of approx. 11 %). One advantage of this technology is that due to the sinter process under shielding gas the framework has no, or only a minimal, oxidation layer. This reduces trimming after sintering to a minimum (Fig. 1 and 2).

Mechanical properties

Following sintering, the alloy achieves mechanical properties that are comparable to those of cast, laser-melted or subtractively processed chrome-cobalt alloys. The mechanical properties of alloys processed in different ways are illustrated in Table 1. The tensile strength (Rm) here indicates the highest stress value achieved during measurement. In the stress-strain diagram it is the last measured point before the test piece breaks. However, this measurement is not of great relevance for dental materials, as plastic deformation is not desired in the patient’s mouth. The decisive parameter in dentistry is the proof stress (Rp 0.2 %). The proof stress indicates the stress which the material can still tolerate without undergoing plastic deformation. As it is very difficult to determine exactly the transition between the elastic and plastic zones, a point was defined at which there had already been a permanent change in length of 0.2 % from the initial length (0.2 % proof stress). Elongation at rupture describes the relative change in length at which a test piece breaks in the tensile test. Hardness describes the resistance with which a solid body opposes the

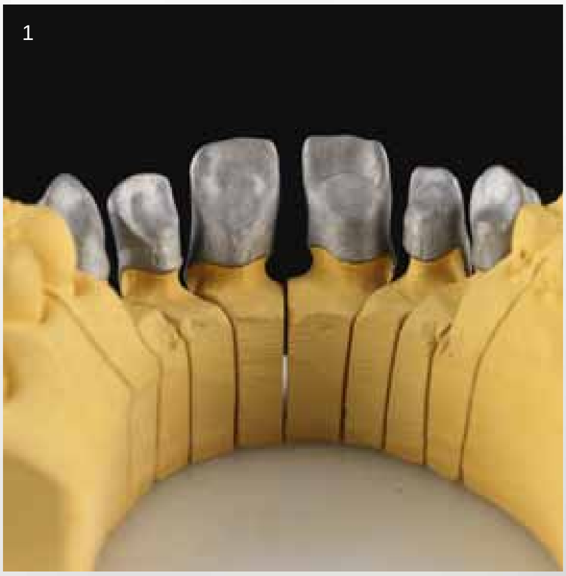


Fig. 1 and 2 Using the new processing technology crown and bridge frameworks can be milled in the usual way from Ceramill Sintron in the green body state. The frameworks achieve their usual material properties in a subsequent sinter process under shielding gas.

indentation of another harder body and the modulus of elasticity, shortened to e-module, is a measurement for the rigidity of a material.

In summary, it can be stated that the chemical composition, appearance, mechanical and biological as well as the processing properties of Ceramill Sintron in the sintered state are comparable in practice to those of CoCrMo casting alloys, which have been used successfully clinically for many years.

For analysis of the structure a three-unit bridge was produced in each of the three Amann Girrbach CoCrMo processing techniques (casting, laser sintering, milling + sintering) and then prepared metallographically.

The cross-sections – one of which and the respective area examined is shown in Figure 3 a – were chemically etched to allow visualisation of the structure. In Figures 3b to 3g the respective structures are shown in comparison and in two magnifications. The considerably smaller and more homogeneously distributed grains are particularly noticeable with the new CoCr material. This difference in size is very impressive, especially compared with the casting alloy.

If it is also taken into consideration that, in general, smaller grains result in increased corrosion resistance and mechanical strength, this new approach to processing CoCr alloys may also be expected to bring about clinical advantages.

Mechanical properties of dental CoCrMo alloys and their composition

	Girobond NB	Ceramill NP L	Ceramill Sintron
Tensile strength (Rm)	850 MPa	800 MPa	830 MPa
0,2% Dehngrenze (Rp0,2)	620 MPa	600 MPa	450 MPa
Modulus of elasticity (E)	210 GPa	170 GPa	200 GPa
Elongation at rupture	10 %	10 %	20 %
Vickers hardness (HV 10)	320	320	280
Coefficient of thermal expansion (25-500 °C)	$14,6 * 10^{-6}$/K	$14.0\text{-}14.5 * 10^{-6}$/K	$14,5 * 10^{-6}$/K
Specific weight	8,5 g/cm³	8,5 g/cm³	8,0 g/cm³
Chemical composition	62 % Co, 25 % Cr, 5 % Mo, 5 % W, 1 % Si, <0.1 % Ce	62-66 % Co, 24-26 % Cr, 5-6 % Mo, 5-6 % W, <1 % Si, <0.1 % Mn, <0.5 % Fe	66 % Co, 28 % Cr, 5 % Mo, <1 % Mn, <1 % Si, <0.5 % Fe

Structure analysis of a three-unit CoCrMo bridge framework

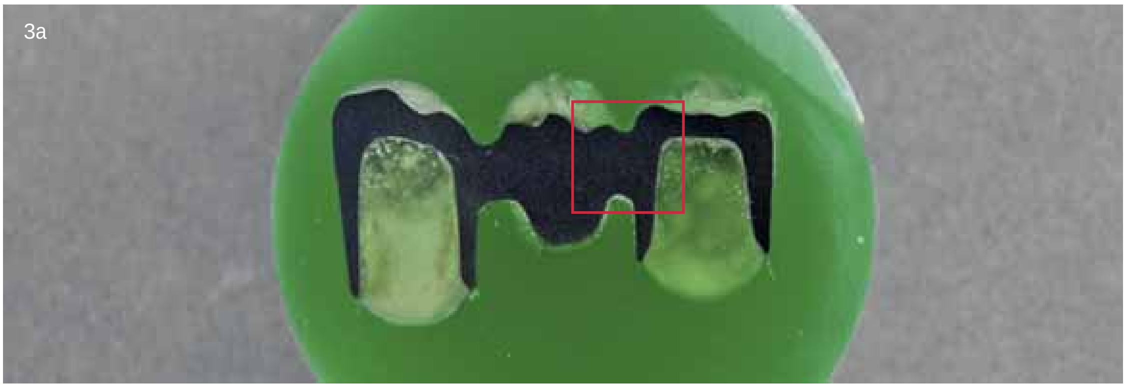


Fig. 3a To examine metallographically the structure of the three CoCrMo processing techniques (casting, laser sintering, milling + sintering) cross-sections and polished test pieces were fabricated from them and each examined in the region shown in the red box.

Fig. 3b Ceramill Sintron (4x)

Fig. 3d Girobond NB (4x)

Fig. 3f Ceramill NPL (4x)

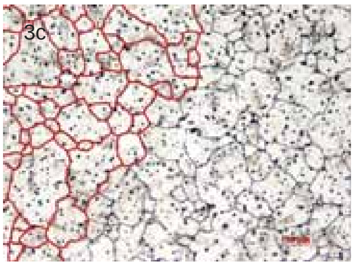


Fig. 3c Ceramill Sintron (200x)

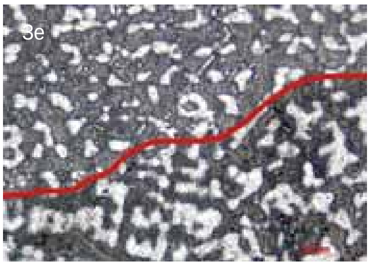


Fig. 3e Girobond NB (200x)

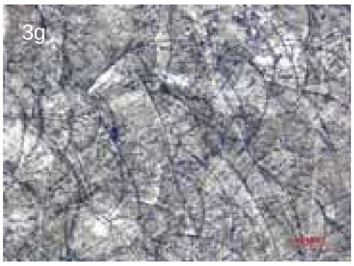


Fig. 3g Ceramill NPL (200x)

Other studies that support this theory will be published shortly. In the structure analysis at 200 times magnification a homogeneous and completely isolated (closed) microporosity is visible, which is typical for free sinter processes. This cannot, however, be compared with the porosities and casting defects which are familiar from the casting technique.

Further processing

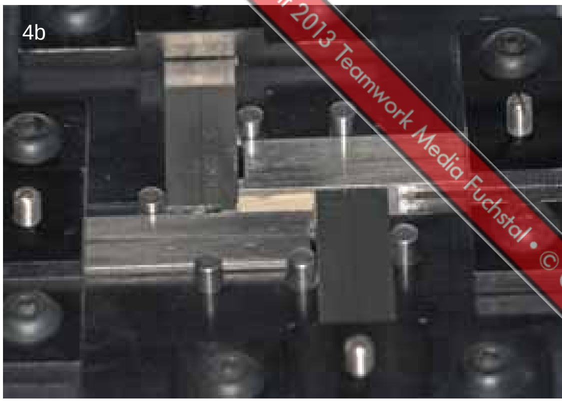
After finishing the Ceramill Sintron frameworks, they can be veneered in the same way as frameworks previously fabricated using CoCrMo casting alloys. Generally, all veneering porcelains that have a suitable coefficient of thermal expansion for non-precious metal alloys can be used for veneering. The bond strength between the framework and veneering porcelain is a decisive factor in the overall strength of the restoration. Apart from the mechanical properties of the framework and veneering material, therefore, the service life of a restoration is determined by a good match between the coefficient of thermal expansion (CTE) of the two bonding materials and the strong strength of the veneering material to the framework material.

Bond strength

To ensure that the practical relevance of the new CoCrMo alloy and its processing technique can be better classified and evaluated, the bond strengths of CoCrMo alloys to three different veneering porcelains were tested. The aim was to test whether the bond strengths to Ceramill Sintron are comparable with the bond strengths of a cast and laser sintered alloy. The CTE values of the three tested CoCrMo alloys were between 14.0 - 14.6 $* 10^{-6}$/K. However, it is not only the coefficient of thermal expansion properties that have an influence on the bond strength but also the mechanical

Fig. 4a
Fabrication of the Schwickerath test pieces according to EN ISO 9693:2000

Fig. 4b
A special device was used to produce a standardised bond surface on the test pieces



and chemical bond. The mechanical bond was achieved here by sandblasting. Consequently all test pieces in this test were sandblasted. The chemical bond forms due to the composition of the alloy. The non-precious components in combination with oxygen form an oxide layer, which bonds directly with the veneering porcelain.
To achieve results that can be compared with existing data, bond strength measurements were conducted according to the EN ISO 9693:2000 standard. Three different veneering porcelains with suitable CTE values were used in this test: Vita VM13 (Vita Zahnfabrik), Willi Geller Creation (Creation Willi Geller International) and Reflex (Wieland Dental + Technik). In addition to Ceramill Sintron, Ceramill NP L laser sinter alloy (Amann Girrbach) and Girobond NB casting alloy (Amann Girrbach) were also used as framework materials. Forty five bases were fabricated from each type of alloy (Fig. 4a) and these were then sandblasted using aluminium oxide (Al_2O_3), grit size 110 µm and a pressure of 3 bar. Three groups of 15 test pieces per veneering porcelain were then formed according to the random principle and these were then veneered according to the respective manufacturer's instructions. A special device was used for fabricating the test pieces to produce a standardised bond surface (Fig. 4b).

After the opaque firing (Fig. 4c), two dentine firings and a glaze firing were completed (Fig. 4d to 4f).

Fig. 4c to 4f
After the opaque firing, two dentine firings were completed

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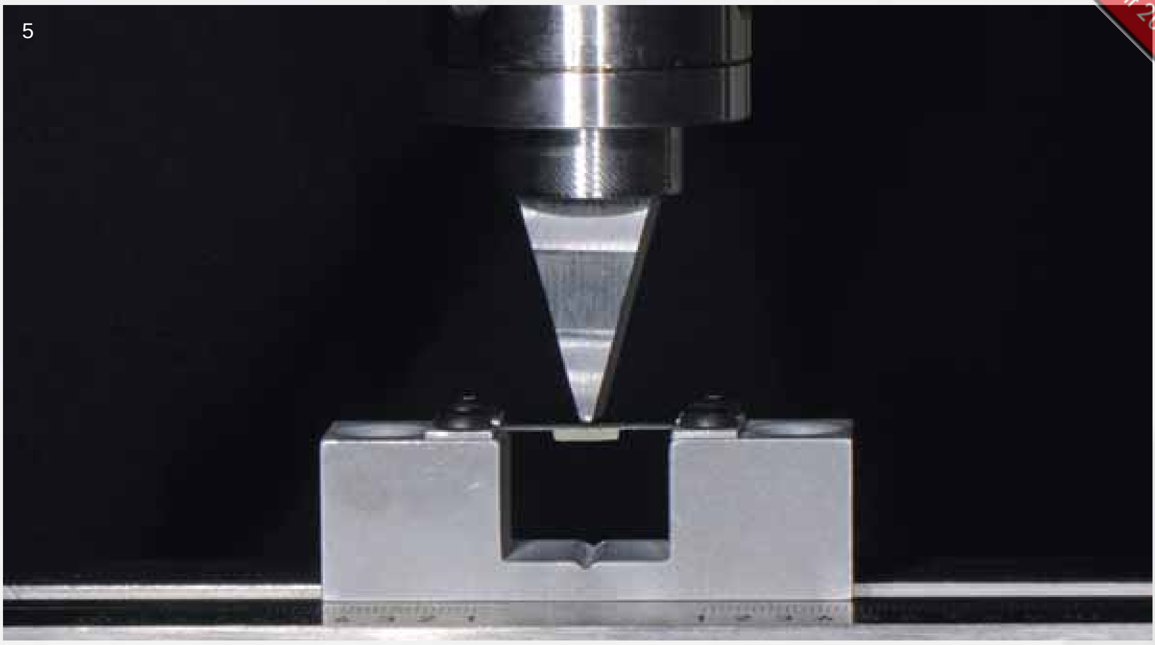

Fig. 5
This picture illustrates an example of the Schwickerath test set-up. The bond strength between the alloy and veneering porcelain is tested here

The test pieces were artificially aged after veneering, as the intention was to simulate the temperature fluctuations that occur in the oral cavity. The test pieces were subjected to 5000 thermocycles between 5 °C and 55 °C for this. These temperature fluctuations could strain the bond between the two materials, as they expand differently due to the different coefficients of thermal expansion.

The bond strength of the test pieces was then tested in the Schwickerath test (Fig. 5). The bond strength values calculated are shown in Figure 6.

There were no significant differences in the bond strength values between the different CoCrMo alloys. In summary, it can be established that Ceramill Sintron bonds just as strongly to veneering porcelains as does a cast or laser sintered alloy.

Comparison of the processing options

If the different processing possibilities of CoCrMo alloys are compared with each other, subtractive processing of a green body with subsequent sintering (Ceramill Sintron) exhibits much fewer sources of error than the conventional casting technique. The structural homogeneity of the industrially manufactured blank is not the only advantage but mainly its composition, which is not altered either during the milling process or the subsequent sinter process. In contrast, potential user errors can influence the quality of the material when casting alloys. In addition, during the casting procedure segregation phenomena may occur in the molten metal due to concentration gradients. Not all alloy components are uniformly and homogeneously arranged in the structure during the solid-

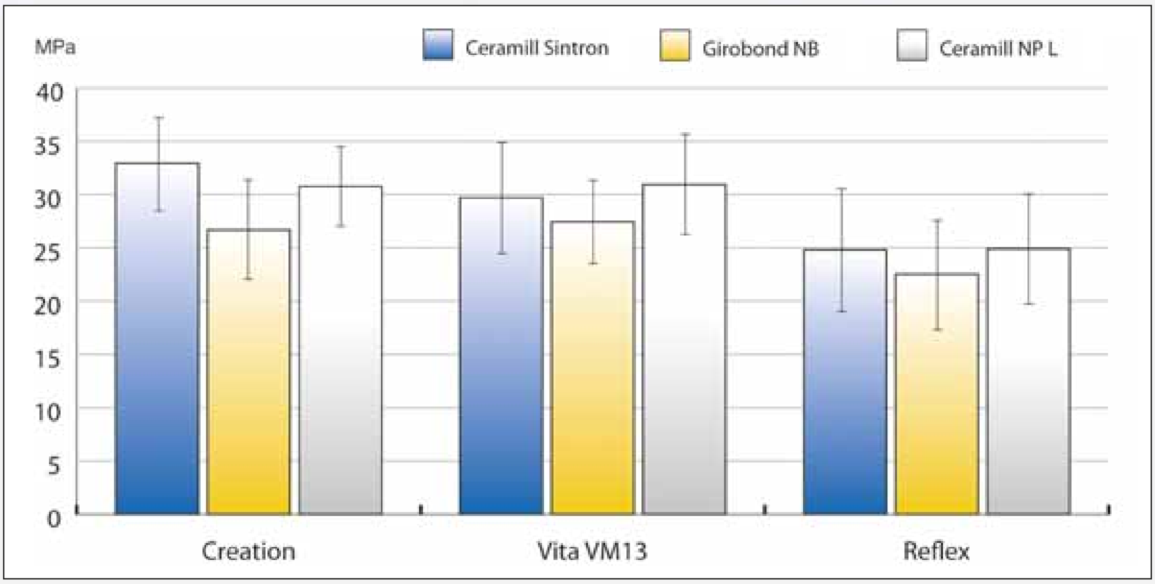

Fig. 6
Bond strengths (MPa) between the different CoCrMo alloys and veneering porcelains

ification process of the molten metal. Certain areas of the structure become impoverished of alloy components while other areas are enriched with alloy components. Excessively high melting temperatures may also cause a reduction of the low-fusing alloys and this can change the composition. In case of inhomogeneous solidification of alloys, different concentrations may occur in the structure in the sense of a galvanic element that could cause localised corrosion processes.

As the Ceramill Sintron blanks are manufactured industrially the processing errors of the alloy are minimal. Further processing errors are also avoided during computer-aided subtractive processing of the green body. Segregation phenomena are not possible or possible only to an extremely limited degree during the sinter process, as sintering involves diffusion-controlled material transport without the creation of a liquid phase. This is also referred to as solid-phase sintering in this context (like the sinter process of zirconia). Any contamination of the alloy, for example by residue of the investment or the prototype material is excluded due to the process. Surface oxidation of the sinter framework is reduced to a minimum because sintering is completed under a shielding gas atmosphere. Up until now the positive effects of computer-aided processing of CoCrMo alloys were reserved for large manufacturing centres. The approach described in this article of processing a green body subtractively and then sintering it is possible on smaller CAD/CAM machines directly in the dental laboratory. In comparison, frameworks fabricated additively using the laser technique are also manufactured externally in laser centres. The new technology allows the fabrication process and consequently the value creation to remain in the dental laboratory.

Conclusion

The possibility of processing the CoCrMo alloy Ceramill Sintron in the dental laboratory with the support of CAD/CAM as well as its mechanical properties make this processing technique very interesting. No compromises are required from users, as it could also be confirmed that the material could be veneered in the usual way in the dental laboratory. The results obtained in this study for the bond strength of framework material and veneering porcelain are equivalent to those of already well-known and applied fabricating procedures for veneer frameworks – referring to the casting technique and selective laser melting in this article.

About the authors

The CV of the authors can be found at www.teamwork-media.de/download/authors/dd9_12_stawarczyk.pdf or directly using the adjacent QR code.

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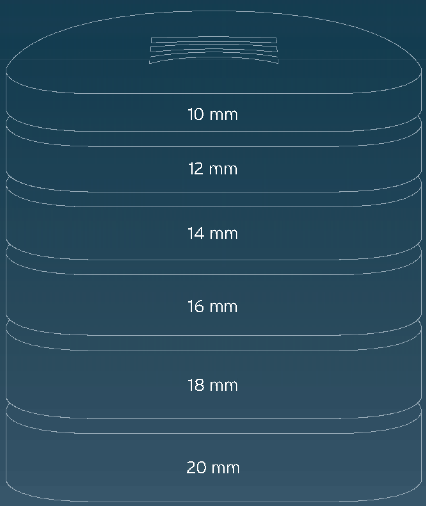
ceramill sintron®

CoCr sinter metal for CAD/CAM dry milling

For the first time Ceramill Sintron® enables CNC-based* dry milling of non-precious metal restorations using desktop milling machines in-house in the laboratory. Up to now it has not been possible to fabricate CoCr restorations on "small" laboratory milling machines because of the material hardness. Due to the "wax-like" texture of the Ceramill Sintron® blanks the material can be easily dry milled in the Ceramill Motion 1 and the Ceramill Motion 2. During the subsequent sinter process with shielding gas flushing the frameworks attain their final state - a non-precious unit with a very homogeneous material structure.



Ceramill Sintron®71

_6 heights of blank (XXS = 10 mm to L=20 mm)

_Expansion factor of approx. 11%

_Developed specially for processing in the Ceramill system

_25 to 30 units can be milled from one Ceramill Sintron blank

Indications:

_Anatomically reduced and fully anatomical crown and bridge frameworks in the anterior and posterior region

_Bridge frameworks with a maximum of two connected pontics in the anterior and posterior region and a maximum anatomical length of 50 mm

_Cantilever bridges with a maximum of one bridge pontic (maximum one cantilever unit up to the second premolar maximum).

Contraindications:

_Known incompatibility to the components

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Comparison of the mechanical properties of a CoCr sinter alloy with a CoCr casting alloy

As good as cast

An article by Prof. Dr. Jürgen Geis-Gerstorfer, Tübingen/Germany, Dipl.-Ing. Falko Noack and Dipl.-Ing. Axel Reichert, both Koblach/Austria, and Christine Schille (PhytA), Tübingen/Germany

Amann Girrbach is putting Ceramill Sintron, a dry millable CoCr material for processing using CNC technology, on the market. This is possible because the material – similar to a partially sintered zirconia blank in dentistry – is in a preliminary state which can be easily processed. After the required frameworks have been milled from the blank they are debinded and densely sintered in a downstream process.The following article is intended to clarify whether the final mechanical properties of Ceramill Sintron are comparable with those of established CoCrMo casting alloys.

Introduction

In times in which all-ceramic restorations are proverbially on everyone's lips, it appears that materials which have been used successfully over many years still retain their high importance as dental restoration materials. Special non-precious metal alloys (NPM) are among the preferred material groups for fabrication of a restoration with a long-term prognosis. This class of alloy has become established in the dental market over decades as a cost-cutting alternative to precious metal alloys due to their good mechanical properties, biocompatibility and porcelain veneering properties etc. Special CoCr alloys are widely used for the fabrication of restorations, particularly if high demands are placed on the strength of the framework.

Processing of non-precious metal alloys up until now has mainly only been possible using the manual casting technique. CoCr frameworks were previously fabricated in the CAD/CAM technique via selective laser melting (SLM) or milling from blanks, which already had the final properties of the material.
The two latter processing options, however, were associated with enormous acquisition costs for the respective production equipment and were therefore mainly reserved for production centres that specialised in industrial fabrication of CoCr restorations.

The easy processing properties of a new CoCr sinter metal blank, which is in a preliminary material state technically as a green body, means that CoCr restorations can now also be fabricated using CAD/CAM in dental laboratories, which do not have industrial standard production machines [1]. The consistency of the blank, which is manufactured in a powder metallurgical process, enables it to be dry milled without additional cooling on milling machines. This easy processing is based on the fact that the blank consists of a powder atomised CoCrMo alloy, whereby the cohesion of the powder particles is guaranteed by an organic binder.

After the milling process (CNC controlled), the framework produced is debinded in a special sinter furnace and densely sintered under a shielding gas atmosphere. The material achieves its mechanical properties on completion of the sinter process, which is accompanied by a volumetric shrinkage of approximately 10 %. The study described below is intended to answer the question of whether the final mechanical properties of the CoCr sinter metal are comparable to those of established CoCrMo casting alloys that have been used successfully over many years in the dental market.

Description

The aim of this materiological study was to compare the mechanical properties of

Fig. 1
Fixed restoration fabricated using Ceramill Sintron CoCr sinter material

Literature

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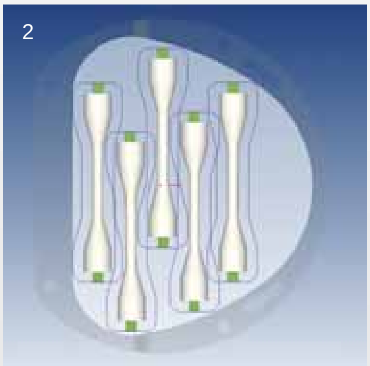


Fig. 2 Using this dataset test pieces were milled from wax and Ceramill Sintron for the tensile test

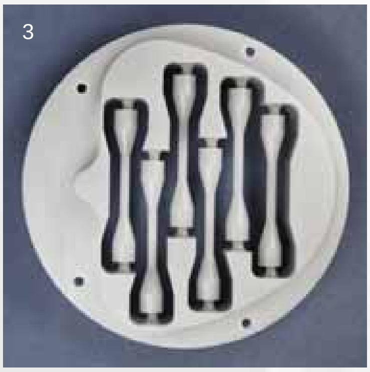


Fig. 3 Tensile test pieces in the wax blank. After separation, the test pieces were sprued, invested and cast using Girobond NB

Fig. 4 The test pieces for the tensile tests, which were milled from the sinter metal Ceramill Sintron in the green body state

conventionally fabricated dental precision castings (Girobond NB) with the properties of a milled and densely sintered sinter metal alloy (Ceramill Sintron). Both non-precious alloys are manufactured and sold by Amann Girrbach. A comparison of the two manufacturing processes of the test pieces required and the analysis of the results are also presented in this article. Both alloys are used for fabricating fully anatomical and anatomically reduced crown and bridge restorations (Fig. 1). As a variety of non-precious metal casting alloys have been used for many years in crown and bridge work, it must be established whether the mechanical properties of a sinter alloy meet the strength requirements for fabricating fixed or removable restorations in accordance with DIN EN ISO 22674 [2].

Fig. 5 The sinter metal is debinded and densely sintered in the special Ceramill Argotherm furnace

Material and method

In order to record all relevant mechanical properties of the two alloys, standardised test pieces were fabricated for performing a tensile test according to DIN EN ISO 22674.

More specifically, six tensile test pieces were fabricated and tested for each alloy and processing technique. CAD/CAM-supported fabrication of the test pieces was based on the respective datasets for milling production (Fig. 2).

The prototypes of the tensile test pieces for the casting alloy Girobond NB were milled from wax blanks (Ceramill Wax, Amann Girrbach) based on the same CAD/CAM dataset (Fig. 3). The Ceramill Sintron test pieces were milled from a corresponding sinter metal blank taking the expansion factor into consideration (Fig. 4). As dental restorations could be fabricated in the same way from both materials, this method of fabricating the test pieces simultaneously takes into account any existing influence of milling on the quality of the test piece. All test pieces were separated from the CAD/CAM blanks after milling and the end faces were trimmed level.

The Ceramill Sintron tensile test pieces were then densely sintered under shielding gas atmosphere (argon) in the Ceramill Argotherm (Fig. 5), which was specially designed for Ceramill Sintron. The test pieces were supported by a layer of beads in the Argovent sintering tray during the sintering process (Fig. 6) and removed in the densely sintered state at the end of the programme.

After separation from the blank, the milling wax test pieces were sprued using appropriate wax wire, placed in a casting ring (Fig. 7) and invested according to the manufacturer's instructions using Giroinvest Super universal investment (Amann Girrbach).

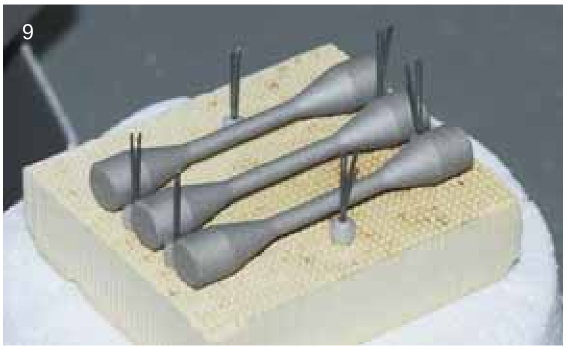
The Girobond NB alloy was also cast according to the manufacturer's instructions using the Heracast IQ (Heraeus Kulzer) vacuum pressure casting machine. After casting, the test pieces were devested, the sprues were cut off (Fig. 8) and then the sprue contact areas were trimmed.

According to DIN EN ISO 22674 bonding alloys must not only be tested with regard to their initial strength values but additional test pieces must also be subjected to heat treatment before testing. The heat treatment corresponds to the sequence of porcelain firing cycles prescribed by the manufacturer for processing the respective veneering porcelain. In the present study the firing cycle values for Creation CC veneering porcelain were used (Creation Willi Geller). The heat treat-

Fig. 6 The Ceramill Sintron tensile test pieces are supported on a layer of sinter beads for sintering

Fig. 7 The milled wax test pieces are sprued and placed in a casting ring for investing

Fig. 8 After cooling, the castings are devested and the sprues are separated from the test pieces



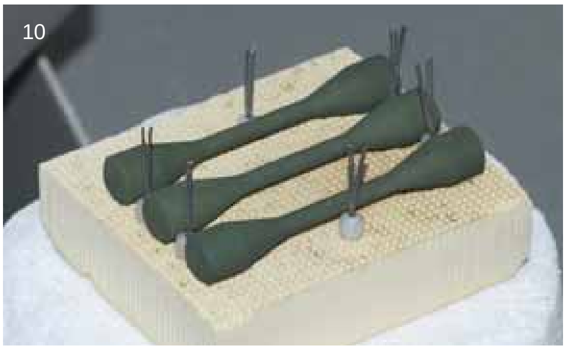


Fig. 9 and 10 Ceramill Sintron tensile test pieces before and after heat treatment

ment required in the strength test is intended to record changes in properties that could be caused by the porcelain firing cycles.

After casting or sintering, the test pieces which were not subjected to heat treatment, were sandblasted using aluminium oxide, grit size 110 µm and cleaned using a steam cleaner. The heat-treated test pieces were subjected to three porcelain firing sequences each with six firing cycles (Fig. 9 and 10). The temperature control of each firing cycle is shown in Table 1. The heat-treated test pieces were also sandblasted and cleaned. The six test pieces of cast and sinter alloy were each identically heat treated.
The DIN EN ISO 22674 standard only requires one firing sequence with an oxide firing and four porcelain firing cycles. In the test described in this article the parameters were intensified due to tripling of the porcelain firing cycles. This procedure was intended to take account of the complete remake of a porcelain veneer, which is sometimes necessary in clinical practice.

Strength test

The tensile test was performed in accordance with DIN EN ISO 22674. To perform the test the tension rods were clamped in the holder of a universal testing machine (Zwick) and pulled apart at a feed rate of 1.5 mm/min. until fracture (Fig. 11).

Hardness test

The hardness was also recorded in the study. Hardness is an important value for

Tab. 1 Firing chart of porcelain firing cycles with which some of the test pieces were heat treated

Firing	Start temperature	Close time	Temperature rate	Vakuum	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	–

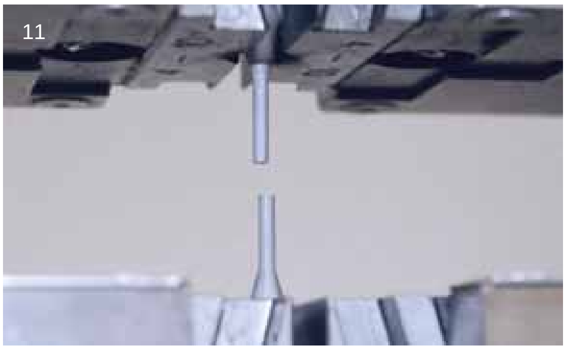


Fig. 11 One of the test pieces after the tensile test. The test piece was pulled apart at a feed rate of 1.5 mm/min. until fracture

Fig. 12 Hardness test according to Vickers on embedded test piece head (hardness testing machine, Frank)

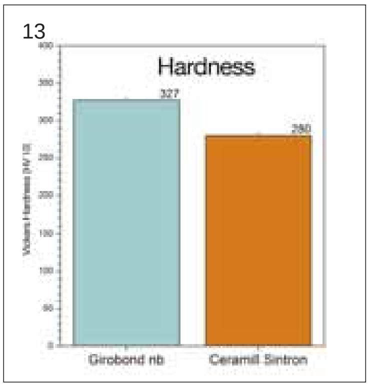


Fig. 13 Comparison of the Vickers hardness HV 10 of Girobond NB and Ceramill Sintron. The Vickers hardnesses of CoCrMo alloys in the literature are between 260 and 380 HV10

the trimming and polishing properties of the material (in the final state). Determination of the Vickers hardness was performed according to DIN EN ISO 6507-1 [3] on both the casting and sinter alloy and compared with one another. The test was performed on metallurgically prepared tension rod heads in each case (Fig. 12).

Results

The results are based on two test series performed in different locations. On the one hand on those of Amann Girrbach, which were ascertained within the framework of the batch test, and on the other hand on those of the strength tests with and without heat treatment. The latter were conducted at Tübingen University Hospital, Germany at the Section of Medical Materials and Technology at the Centre of Dentistry, Oral Medicine and Maxillofacial Surgery.

Hardness

The hardness of Ceramill Sintron is 280 HV10, which is approximately 50 HV10 below that of the Girobond NB casting alloy that was used as a comparison (Fig. 13).

This result is regarded as positive for the sinter material because if the hardness is too high, trimming and polishing is difficult for the dental technician. According to the literature the Vickers hardnesses of CoCrMo alloys are in a range of 260 to 380 HV10 [4]. The value for Ceramill Sintron is therefore at the lower limit of the CoCrMo class of alloys. An improved polishability, as can be attested for the material, has a positive effect on the surface quality of the dental restoration that can be achieved during preparation both in the dental laboratory and the dental practice. A high surface quality with a minimal depth of roughness counteracts increased abrasion on the opposing dentition. A high surface quality is therefore the best protection against non-physiological wear of the natural teeth, which occurs in direct contact with a dental restoration.

Strength

Stress-strain diagrams were created from all tensile strength measurements. The diagrams of Girobond NB (Fig. 14) and Ceramill Sintron (Fig. 15) both following simulated porcelain firing are presented in this article as examples.

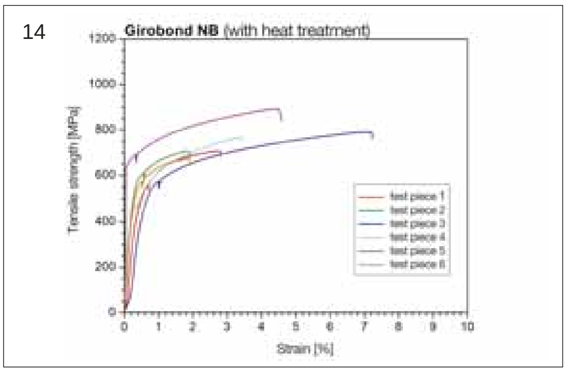


Fig. 14 Stress-strain diagrams of the six Girobond NB tension test pieces

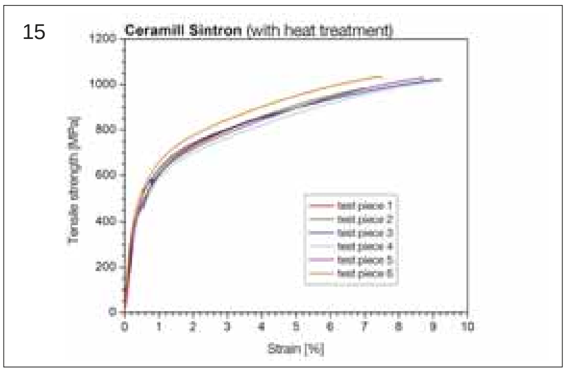


Fig. 15 Stress-strain diagrams of the six Ceramill Sintron NB tension test pieces

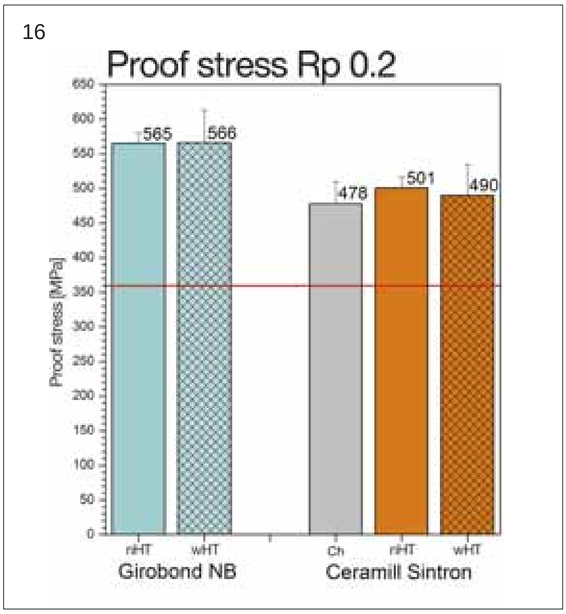


Fig. 16
Proof stress Rp 0.2. The red line represents the minimum requirement of the 0.2 % proof stress for Type 4 alloys

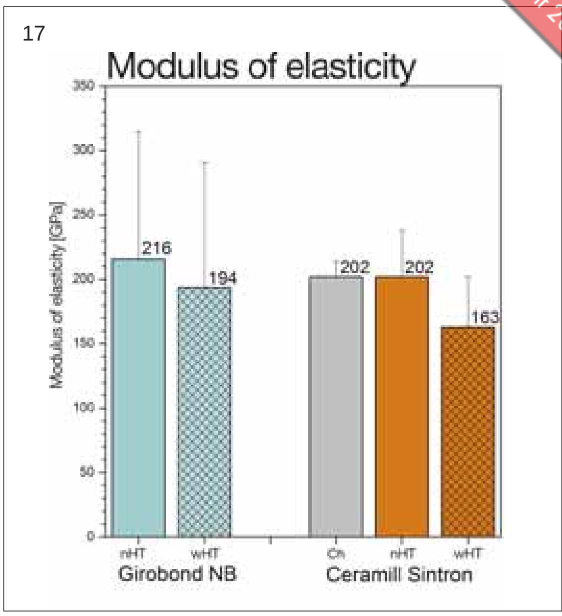


Fig. 17
The modulus of elasticity of different test pieces. nHT stands for "no heat treatment", wHT for „with heat treatment" and Ch denotes the value of the batch control from Amann Girrbach

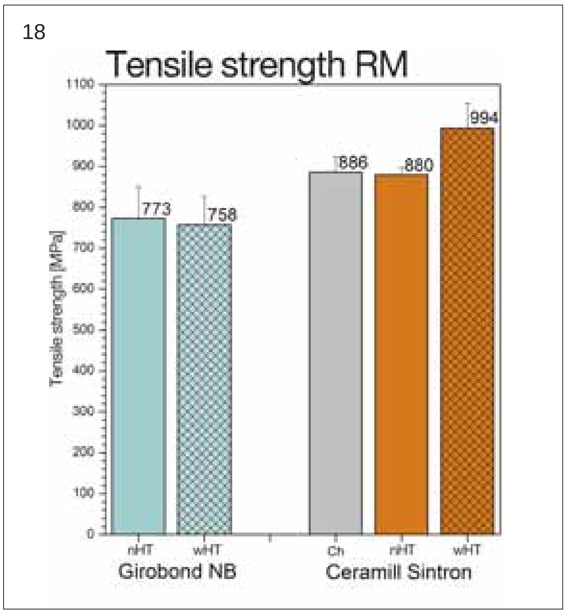


Fig. 18
The values recorded for the tensile strength. The mean tensile strength of Ceramill Sintron is approximately 100 MPa higher than that of Girobond NB

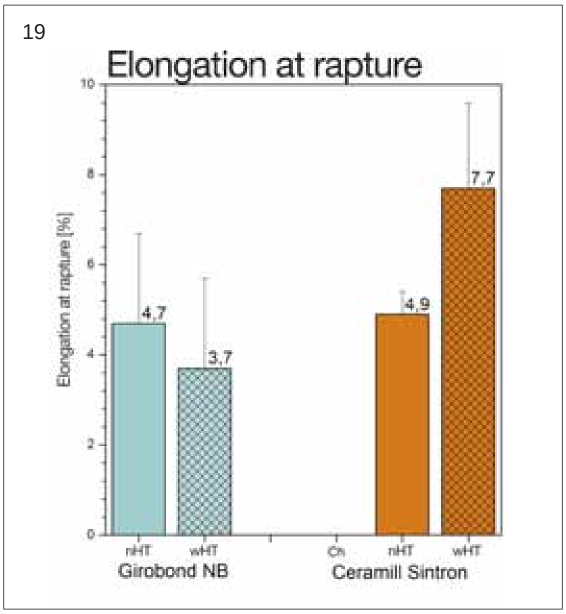


Fig. 19
The elongation at rupture of Ceramill Sintron is higher than that of Girobond NB casting alloy and increases significantly statistically due to the heat treatment

The parameters elongation at rupture A5, proof stress Rp 0.2, tensile strength Rm and the modulus of elasticity were evaluated in accordance with DIN EN ISO 22674.

The mechanical properties can be found in Figures 16 to 19. The results of Girobond NB casting alloy are always shown on the left and on the right are the results of Ceramill Sintron sinter alloy without and with heat treatment (nHT, wHT) and also the data of the batch test (Ch) from Amann Girrbach.

A very important parameter is the 0.2 % proof stress (Rp 0.2), which represents the transition from elastic to plastic deformation. According to DIN EN ISO 22674 Type 4 alloys must have a minimum value of 360 MPa. This is greatly exceeded by both alloys (cf. red line in Fig. 16). The mean values of Girobond NB are slightly higher than those of Ceramill Sintron. No influence of the heat treatment (simulated porcelain firing) on the proof stress was established with either material.

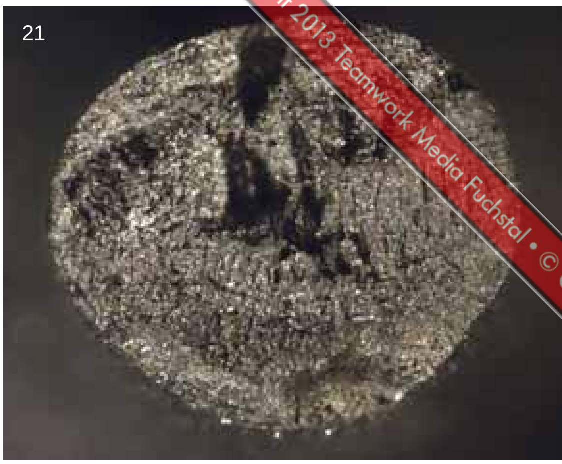
The modulus of elasticity denotes the material-specific resistance against deformation. This means that a material with a higher modulus of elasticity is stretched to a lesser extent when subjected to tensile stress [5], whereby more slender designs are possible, for example in the case of bridge connectors. Girobond NB and Ceramill Sintron exhibit comparable values in this respect (cf. Fig. 17). The mean value of Ceramill Sintron reduces slightly from 202 to 163 GPa as a result of heat treatment. In comparison a typical precious metal alloy is in the region of 110 MPa [6].

The mean tensile strength of Ceramill Sintron is approximately 100 MPa higher than that of Girobond NB and increases further as a result of heat treatment (cf. Fig. 18).

The elongation at rupture of Ceramill Sintron is higher than that of Girobond NB casting alloy and becomes significantly greater statistically due to the heat treat-

Fig. 20
Light microscopic image of an example of a Ceramill Sintron fracture surface (25x magnification) with homogeneous structure

Fig. 21
Light microscopic image of an example of a Girobond NB fracture surface (25x magnification), the structure appears very irregular



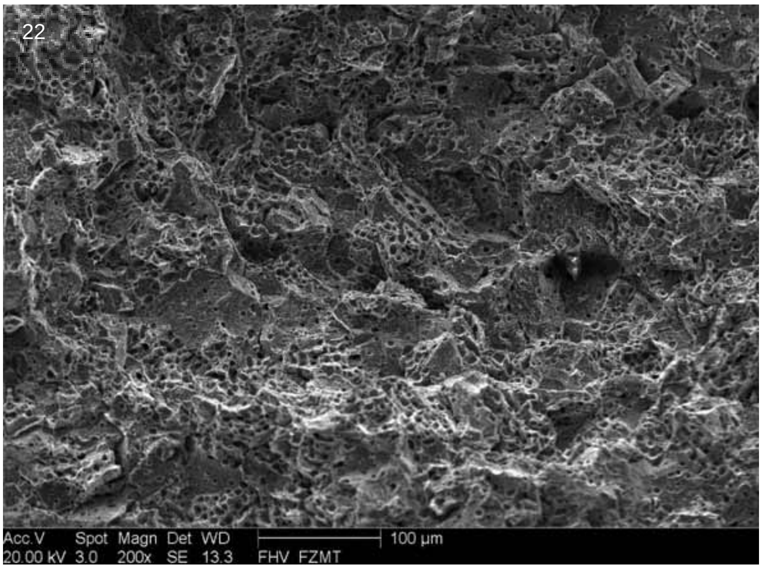


Fig. 22 Scanning electron microscopic image of a Ceramill Sintron fracture surface (without heat treatment, 200x magnification). This image highlights the homogeneity of the fracture surface

ment (cf. Fig. 19). This can be attributed to tension release of the sinter structure.

Microscopy

Images of the fracture surfaces were produced after the tensile tests. The fracture surfaces of Ceramill Sintron (Fig. 20) exhibited a more homogeneous structure in comparison with Girobond NB casting alloy (Fig. 21) (the Figures serve as an example for the fracture surfaces of the other test pieces).
The structure is further emphasised by the scanning electron microscopic image (Fig. 22).

Conclusion

The Ceramill Sintron test pieces which were subjected to heat treatment (similar to a standard firing programme) have the highest elongation at rupture and tensile strength. These are followed by Ceramill Sintron without heat treatment and Girobond NB with and without heat treatment.

In summary, it can be stated that in comparison with Girobond NB casting and bonding alloy Ceramill Sintron sinter alloy has comparable and, in the case of some parameters, even superior strength properties.

There are also similar evaluations in a comparison of laser-melted alloys with cast bonding CoCr alloys (for example [7, 8]). It can be concluded from the present results and the assessment of the SLM structures that production procedures such as laser melting and milling in the green body state with subsequent sintering can replace conventional casting procedures and that they also represent a logical step towards the digital workflow using alloys.

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The CV of the authors can be found at www.teamwork-media.de/download/authors/dd10_12_geis-gerstorfer.pdf or directly using the adjacent QR code.

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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.

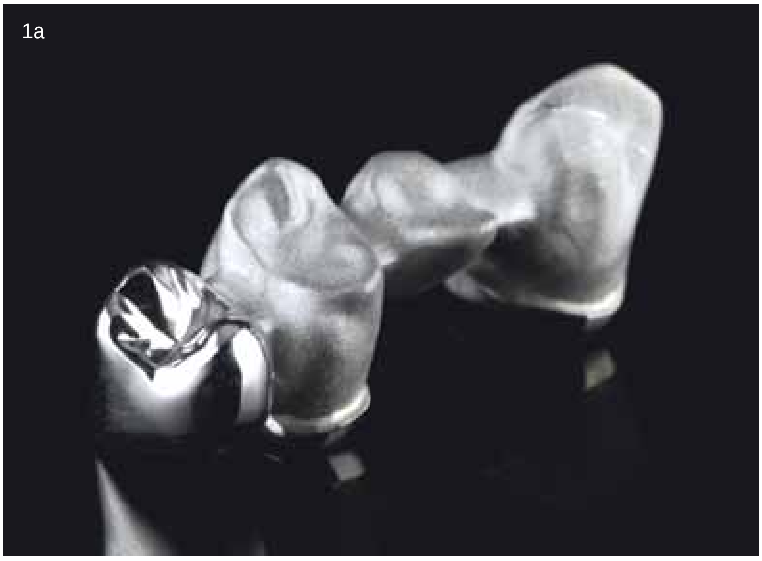

Fig. 1a Dental restorations ...

Literature

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* 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

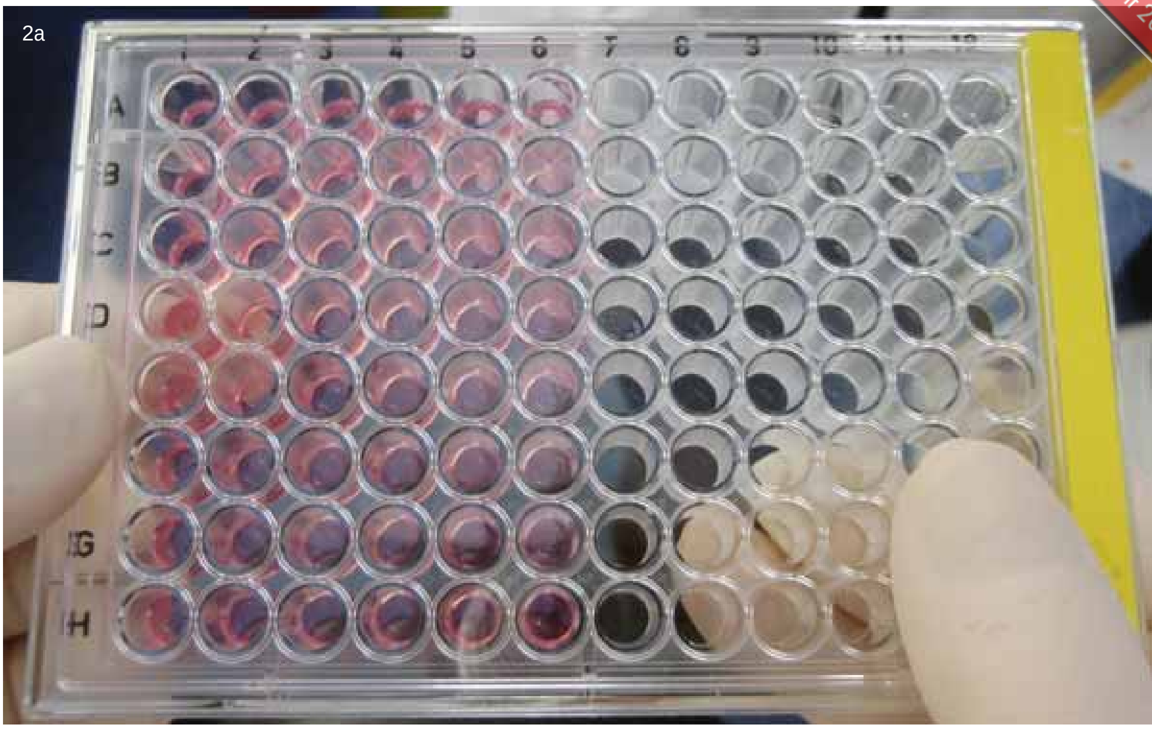


Fig. 2a
The cytotoxicity is ascertained in cell culture tests. …

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 abovenamed 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

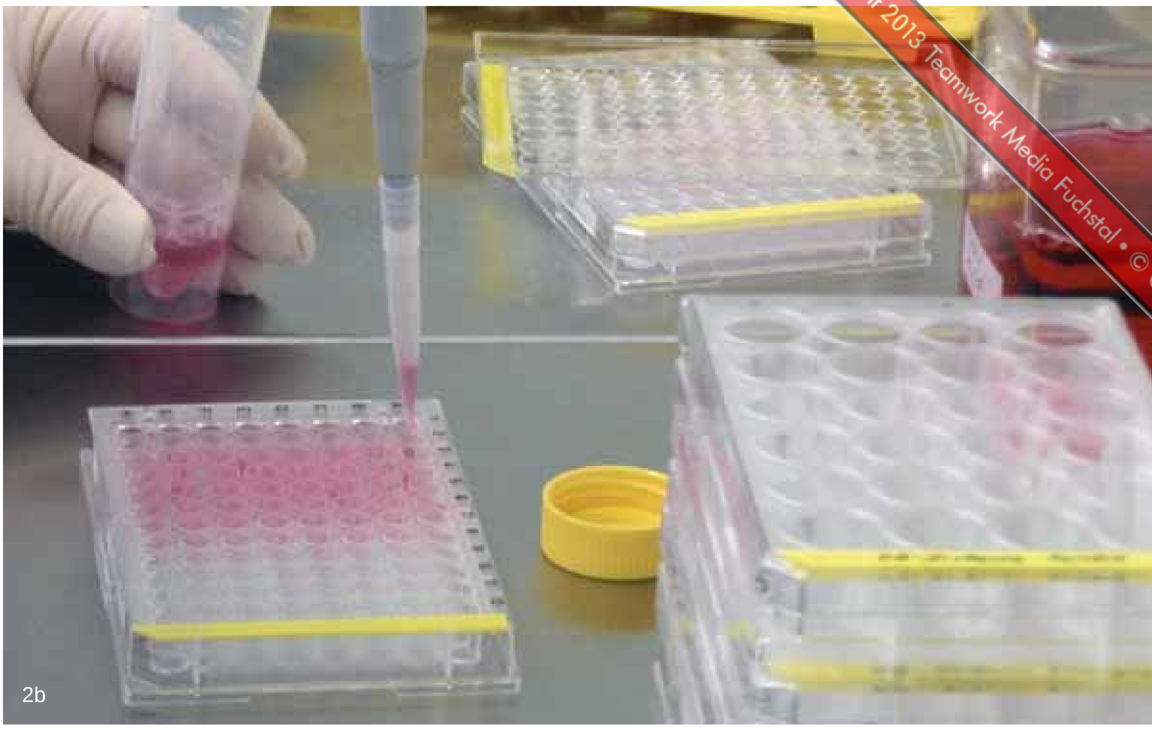
The spectrum of biological hazards is a comprehensive and extensive subject area because of the abundance of existing and offered medical products nowadays. The DIN EN ISO 10993 series is an extensive set of rules that contributes to the protection of humans against possible biological risks when using 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 1200 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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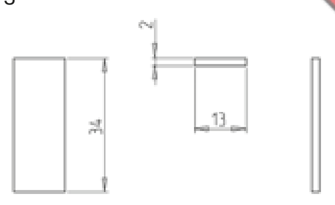

Fig. 3 Design drawings of the test pieces for the static immersion test for examining the corrosion properties

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

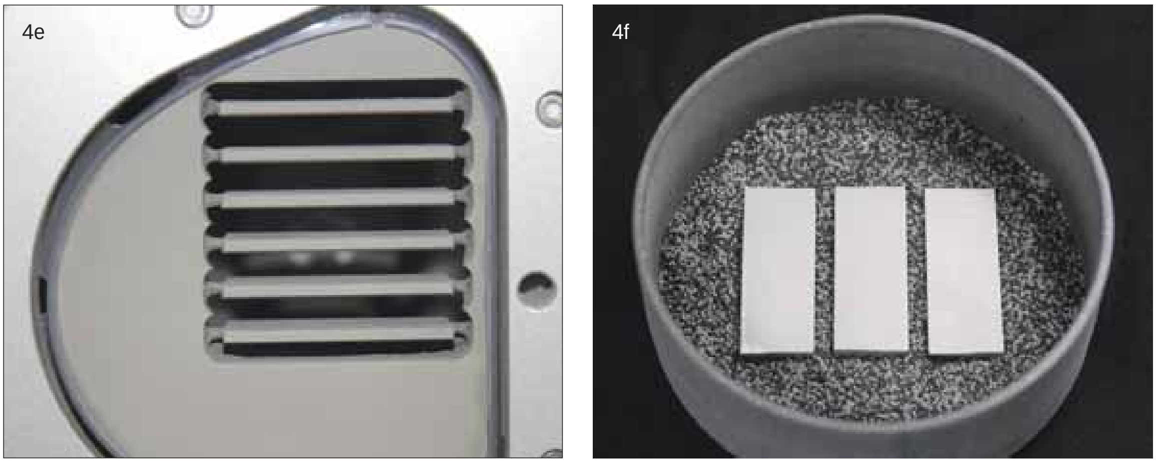

Fig. 4e and 4f The Ceramill Sintron test pieces were based on the same CAD dataset as the Girobond NB test pieces. However, after milling the test pieces were separated from the blank and densely sintered

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.

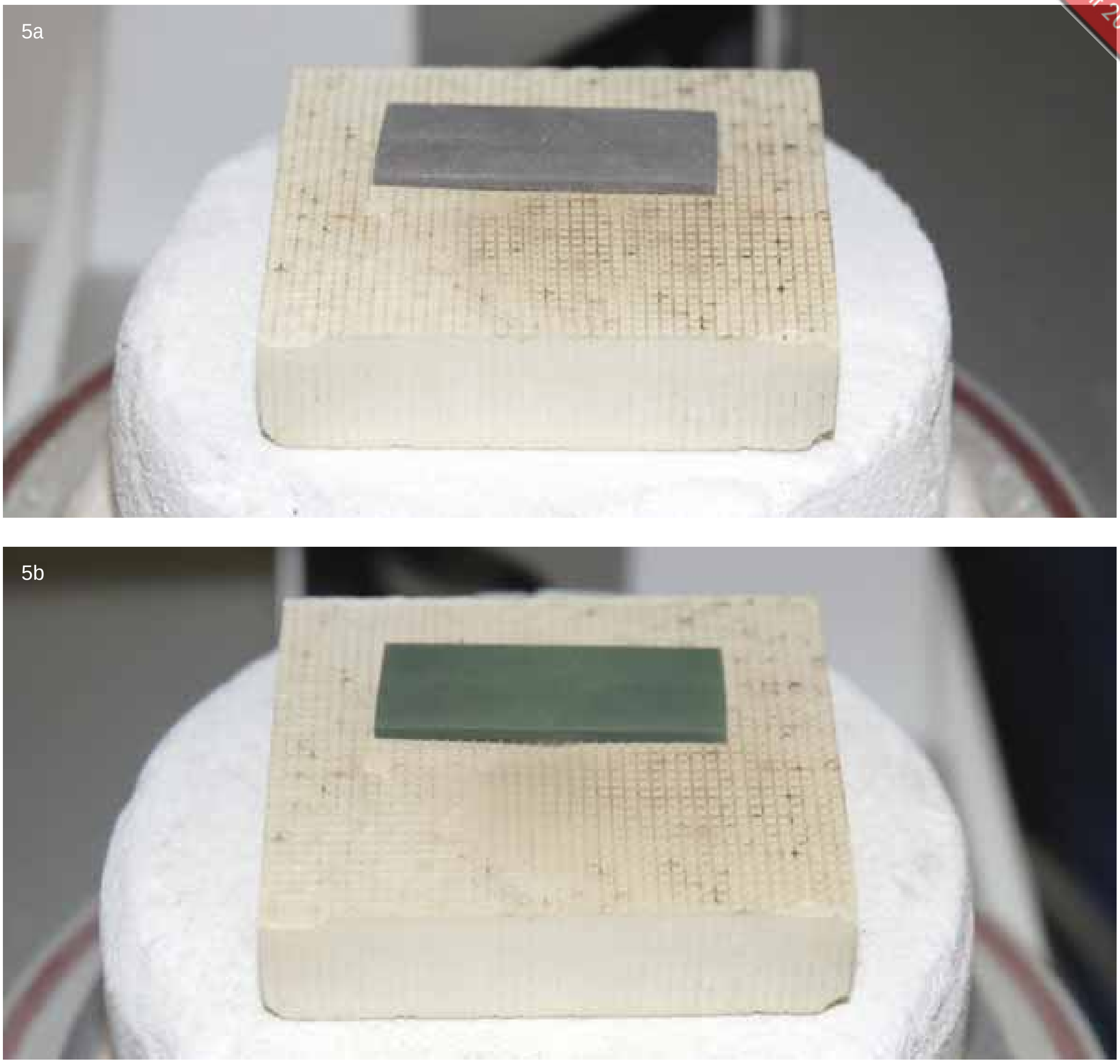

Fig. 5a and 5b According to the present standards alloys, which are also suitable for bonding porcelains, should also be tested in the heat-treated state

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

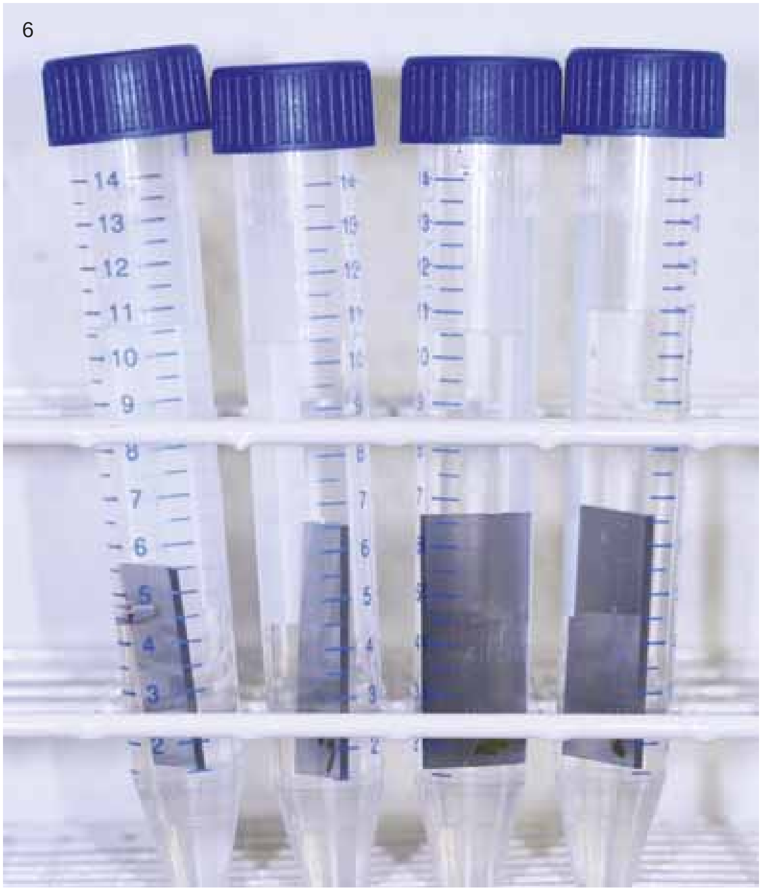

Fig. 6
The test pieces are immersed in 10 ml artificial saliva for testing and determining the corrosion properties

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.

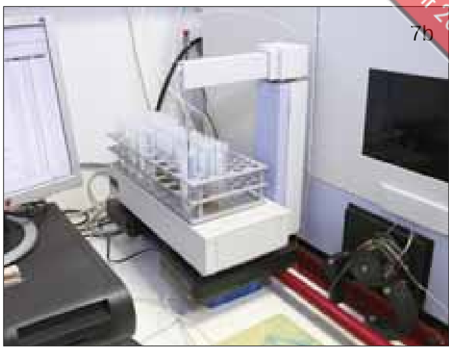

Fig. 7a and 7b ICP spectrometer used for analysis of the metal ions released into the solution and determination of the loss of mass

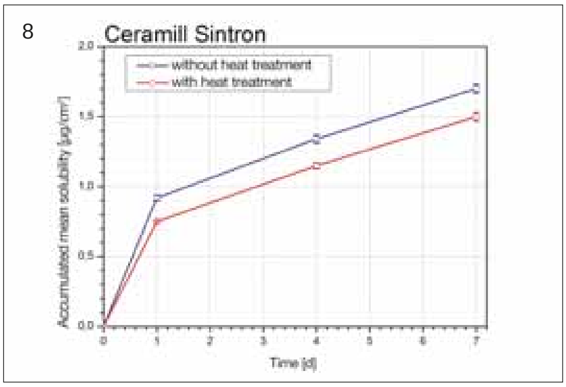

Fig. 8 Accumulated mean loss of mass of Ceramill Sintron over seven days of immersion in artificial saliva

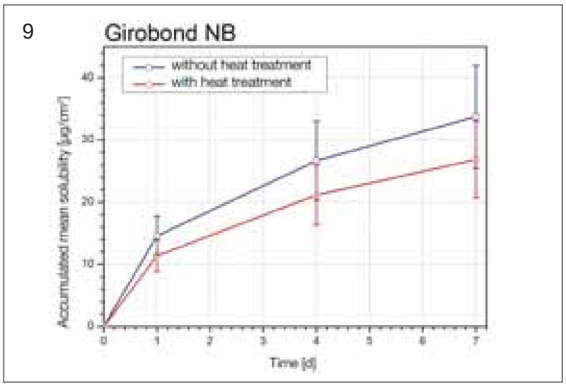

Fig. 9 Accumulated mean loss of mass of Girobond NB over seven days of immersion in artificial saliva

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

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

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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