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

Quickly milled, reliably veneered

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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

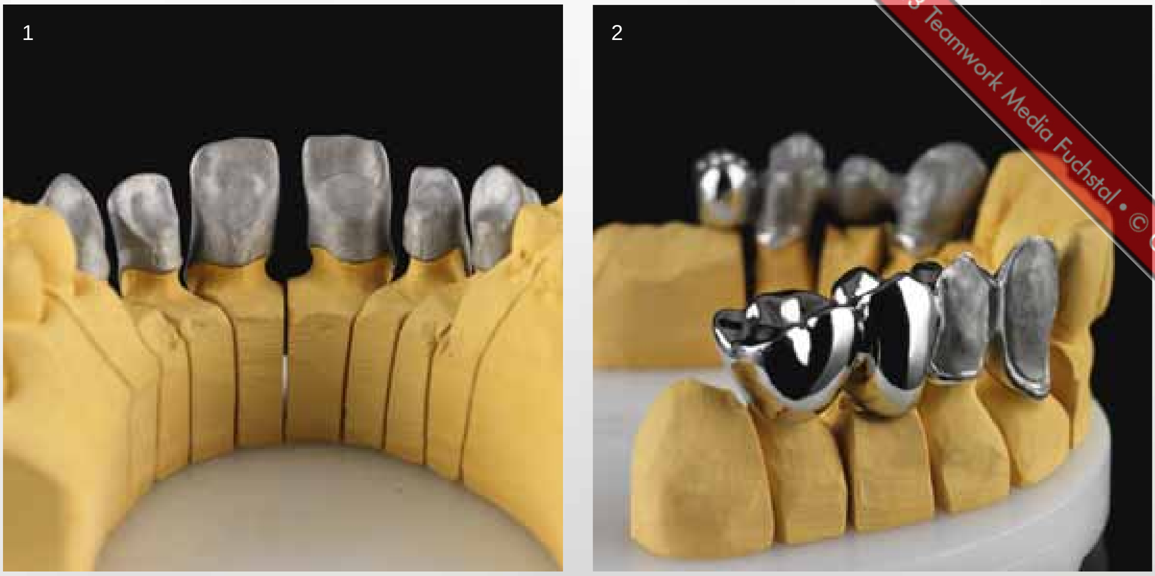


Fig. 1 and 2 Using the new processing technology crown and bridge frameworks can be milled in the usual way from Ceramill Sintron in the green body state. The frameworks achieve their usual material properties in a subsequent sinter process under shielding gas.

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	14.0-14.5 * 10^{-6}/K	14,5 * 10^{-6}/K
Specific weight	8,5 g/cm^3	8,5 g/cm^3	8,0 g/cm^3
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

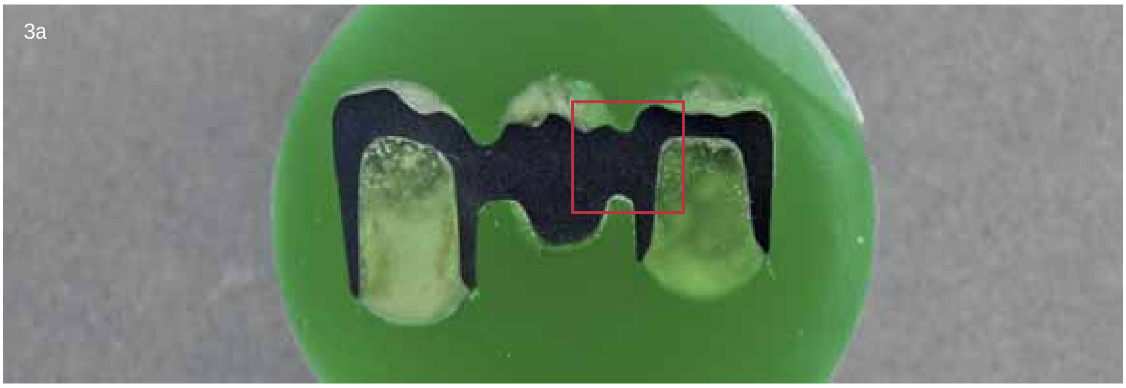


Fig. 3a To examine metallographically the structure of the three CoCrMo processing techniques (casting, laser sintering, milling + sintering) cross-sections and polished test pieces were fabricated from them and each examined in the region shown in the red box.

Fig. 3b Ceramill Sintron (4x)

Fig. 3d Girobond NB (4x)

Fig. 3f Ceramill NPL (4x)

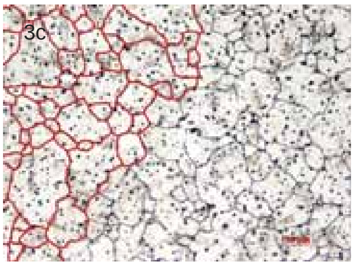


Fig. 3c Ceramill Sintron (200x)

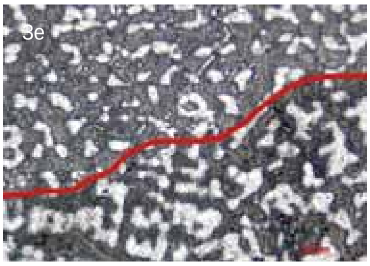


Fig. 3e Girobond NB (200x)

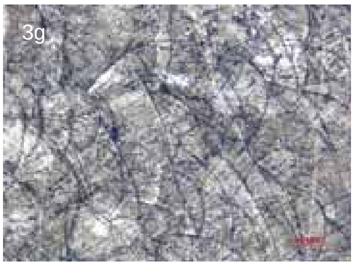


Fig. 3g Ceramill NPL (200x)

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 $14.0 - 14.6 \ast 10^{-6}$/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

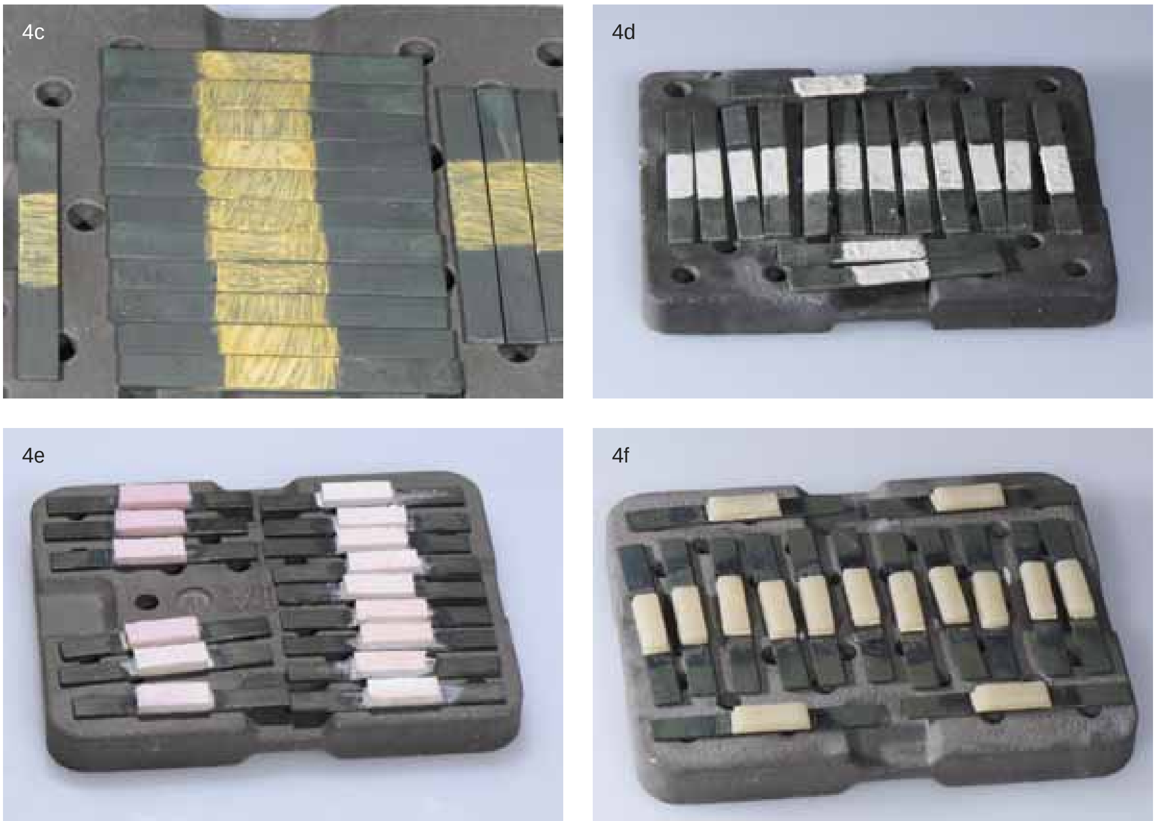
Fig. 4b
A special device was used to produce a standardised bond surface on the test pieces

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



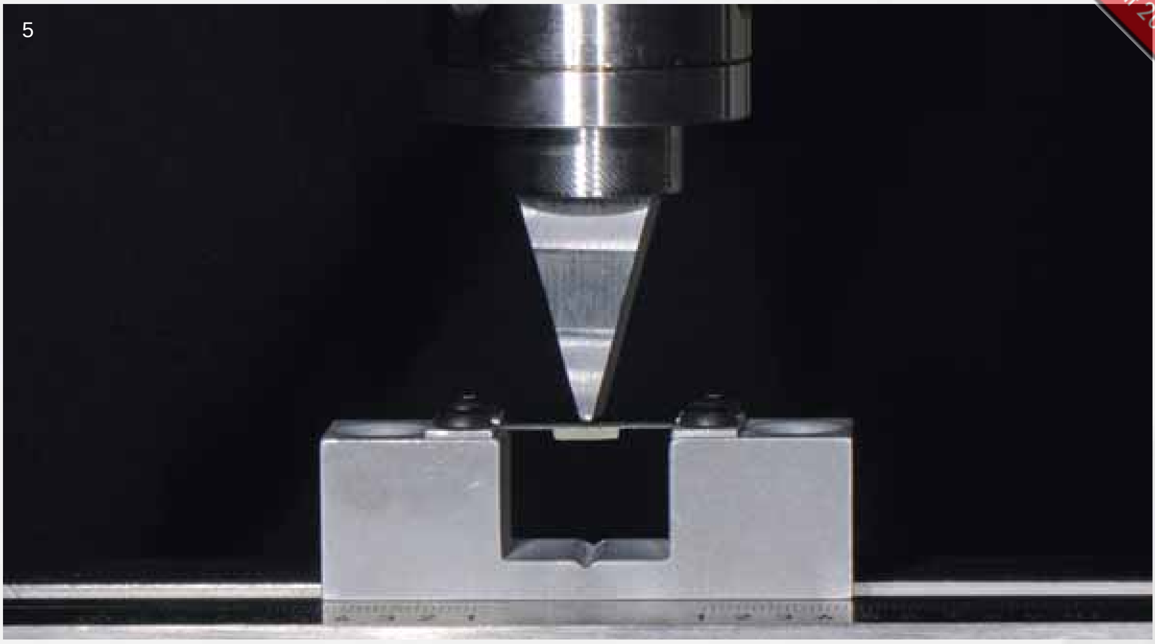


Fig. 5
This picture illustrates an example of the Schwickerath test set-up. The bond strength between the alloy and veneering porcelain is tested here

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-

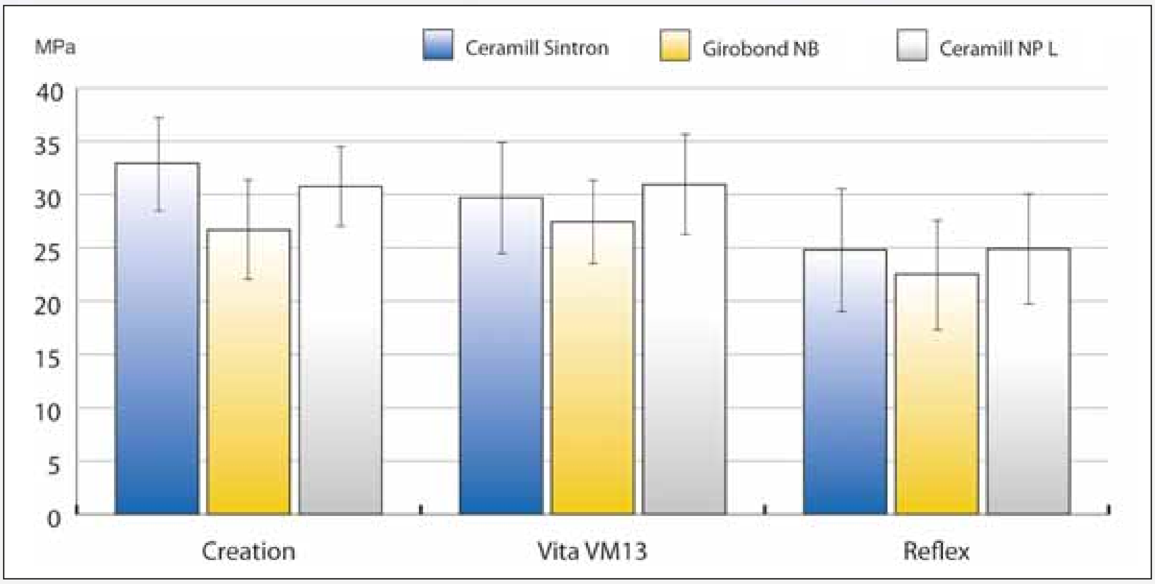


Fig. 6
Bond strengths (MPa) between the different CoCrMo alloys and veneering porcelains

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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