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CoCr Based Alloys in Current Dental Prosthetic Applications

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Abstract. CoCr alloys are traditionally manufactured by casting, but nowadays alternatives such as CAD/CAM milling or 3D Printing Technologies (Direct metal laser sintering (DMLS), Selective laser sintering (SLS), Selective laser melting (SLM), Electron beam melting (EBM)) are available. CoCr blanks to be milled in the green body state (unsintered metal powder held together by a binder) and then densely sintered try to overcome the hardness of the alloy and to ease the milling process.
The aim of this paper is to compare the quality of prosthetic pieces manufactured by CAD/CAM milling, CAD/CAM sintering and Selective laser sintering.
Because the chemical composition of the CoCr alloys used is comparable, differences in quality of the prosthetic pieces are the result of the manufacturing technology. In terms of structure and corrosion resistance, the CAD/CAM milling sample proved to be the best choice and the SLS sample the worst.

1. Introduction

CoCr alloys, which are more often used in dentistry, represent an alternative to NiCr alloys, known as potential allergens. [1,2] Because attempts to produce better dental alloys, e.g. CoCr based alloys dopped with precious metals, were quite a disappointment [3,4,5], nowadays manufacturers are trying to alternatively improve the technological process.

It is well known that CoCr alloys have excellent corrosion resistance, being mainly used for manufacturing removable partial dentures and metal ceramic fixed partial dentures, which involve accurate frameworks. [3,6] Unfortunately, the high hardness makes them difficult to handle both for the dental technician and the dentist, when traditionally manufactured by casting. Casting uses bulk metal, it is laborious and time consuming. When specific flowing parameters of the casting device are not properly set, castability problems and porosities may frequently appear.

New technologies which ease the manufacturing of CoCr alloys are now available:

1. Milling (origin: bulk metal)

CAD/CAM milling technology is based on a virtual impression or a 3D image. The CAD software virtually designs the prosthetic piece and the unit connected to the computer actually mills it. This is quite a hard task in case of CoCr blanks, high demands such as coolant delivery, rigidity of the machine, being placed on the milling device. [6]

A great improvement was made by using units with 4 or 5 axes which permit milling and dry or wet grinding of very good quality prosthetic pieces. Milled elements do not show structure defects such as porosities or cracks.

2. CAD/CAM sintering (origin: powder)

This new technology uses metal blanks with a wax-like texture which allows easy dry milling using system's units. These CoCr blanks are similar to partially sintered zirconia blanks and can be easily milled in this green body state (unsintered metal powder held together by a binder). [7] Afterwards they are debinded and densely sintered in a special furnace. The result apparently has a homogeneous structure. Distortion-free frameworks without contraction cavities are usually obtained. [8]

3. 3D Printing Technologies (origin: powder)

CoCr alloys may be manufactured by using the following 3D Printing technologies:

- Selective laser sintering (SLS) which uses a high power laser to fuse small particles of metal powder into a desired 3D object. Based on a virtual image, the CoCr alloy powder is slowly added, layer by layer, as the 3D CAD software measures thousands of cross-sections to determine exactly how each layer of the prosthetic piece is to be constructed. [9]

The adjustable platform the pieces are built upon moves itself to a height equal to the thickness of each layer that is being built. After scanning each cross-section, the powder bed is lowered by one layer thickness. Additional powder is than added on top of previous solidified layer and sintered. The powder is maintained at an elevated temperature so that it fuses easily upon exposure to the laser. [10]. The SLS technique enables obtaining accurate prosthetic pieces with proper mechanical properties. [9]

- Direct metal laser sintering (DMLS)

In this case the metal powder, with no binder or fluxing agent, is melted by a high power laser beam. The absence of the polymer binder avoids the burn-off and infiltration steps, the result being a piece with higher density and detail resolution compared to SLS. [10]

- Selective laser melting (SLM) uses a high powered laser to melt metallic powders together, followed by heat treatment and post processing. [10]

- Electron beam melting (EBM) uses an electron beam in a high vacuum to melt the metal powder layer by layer. The pieces obtained using EBM are dense, extremely strong and void-free. [10]

2. Experimental part

CoCr alloys for milling, CAD/CAM sintering and SLS were analyzed. Their composition (as given by the manufacturer) shows no great difference, being comparable to that of CoCr alloys for casting. CAD/CAM sintering alloy blanks contain an additional organic binder.

The CoCr samples were embedded in a cold-curing resin on a methyl methacrylate basis, then polished. Electrolytic etching was performed. A metallographic microscope was used for observing the microstructures of the alloys and a scanning electron microscope equipped with an EDX system for local phase analysis and microanalysis was also used.

2.1 Milling (origin: bulk metal)

In figures 1-3 the micrographic structures of the CoCr alloy without and with chemical attack are shown. There are no abnormalities to be noticed, the images being specific for CoCr alloy bulk structures.

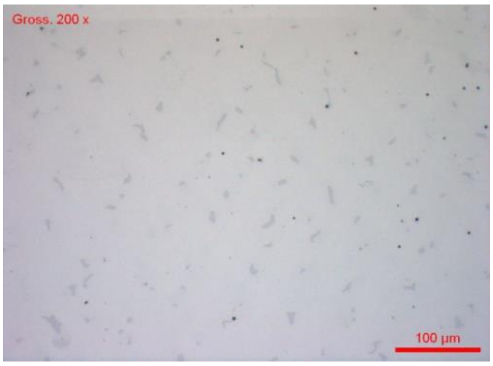

Figure 1. Micrographic structure of the CoCr alloy without chemical attack.

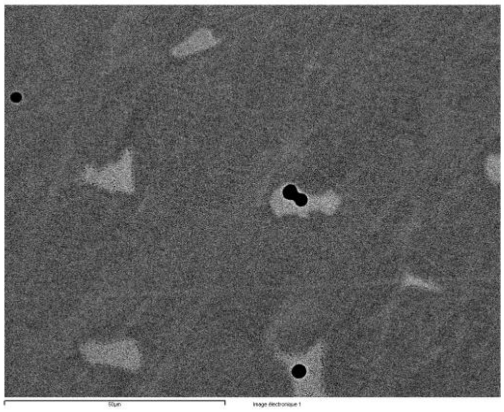

Figure 2. SEM observation of the CoCr alloy without chemical attack.

The chemical composition of the phases is shown in Table 1.

Table 1. The chemical composition of the phases.

Spectrum	C	O	Al	Si	Cr	Mn	Fe	Co	Mo	Total
Spectrum 1: matrix				0.85	28.45		0.85	64.46	5.38	100.00
Spectrum 2: white phase				1.07	38.61		0.38	35.48	24.46	100.00
Spectrum 3: inclusion	14.37	37.13	0.47	17.74	12.26	1.18		14.72	2.13	100.00

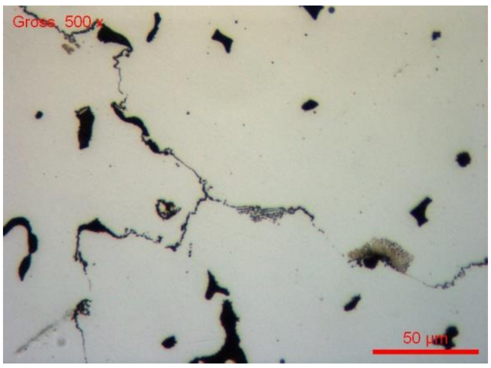

Figure 3. Micrographic structure of the CoCr alloy after chemical attack.

2.2 CAD/CAM sintering (origin: powder)

The micrographic structure without chemical attack shows micrometric porosities, homogeneously distributed, with no noticeable significant defects. (Figure 4)

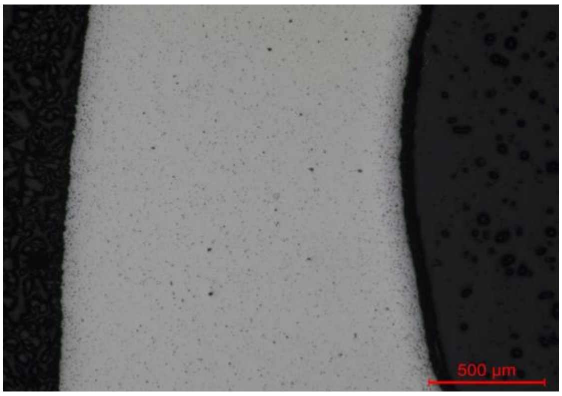

Figure 4. Micrographic structure without chemical attack.

After sintering, the fine and homogeneous microstructure reveals micrometric porosities, homogeneously distributed, typical for sintered pieces. (Figure 5)

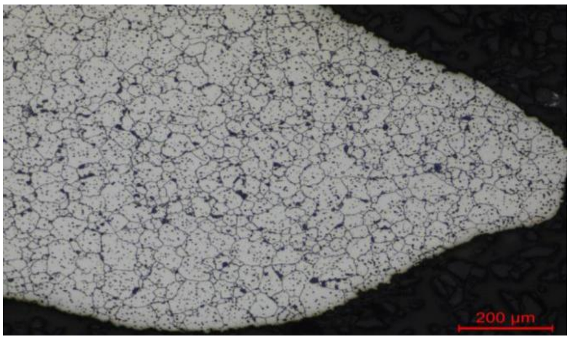

Figure 5. Microstructure after sintering.

2. 3 Selective laser sintering (origin: powder)

The structures examined in vertical and horizontal samples are shown in figures 6-7.

Figure 6. Metallographic observation of a vertical sample.

Figure 6 (vertical sample) shows CrCo piles which are the result of the laser action when building the prosthetic piece.

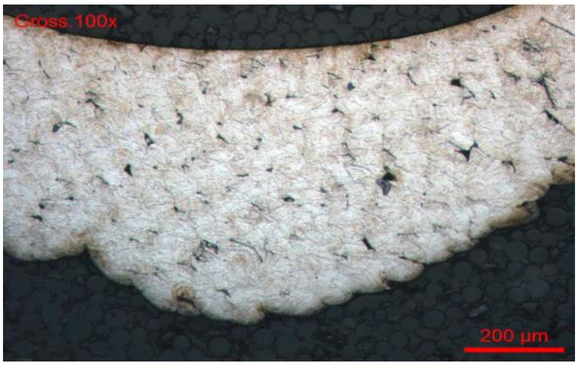

Figure 7. Metallographic observation of a horizontal sample.

The horizontal samples show porosity in the structure of CoCr layers (Figure 7) so further corrosion tests were made, namely electrochemical evaluation by potentiodynamic polarisation in artificial Fusayama saliva (composition: NaCl 0.4 g/l; KCl 0.4g/l; NaH_2PO_4* H_2O 0.69 g/l; $CaCl_2$*H_2O 0.79 g/l and urea 1.0 g/l.) at aconstant 37°C temperature and pH 5.

Scanning electron microscopy (SEM) examination of the sample surface after the corrosion test shows cracks. (Figure 8)

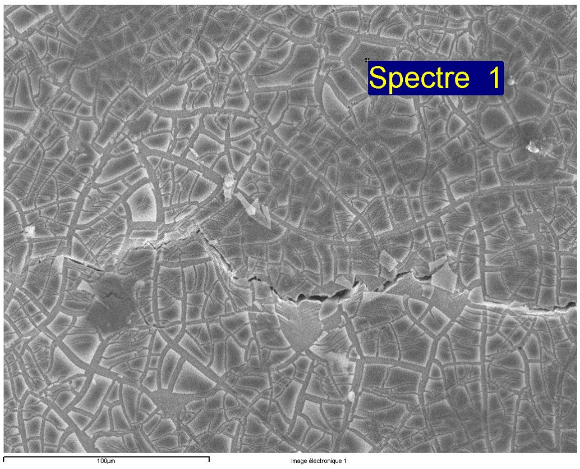

Figure 8. SEM micrograph of the corroded surface after the polarization test.

The spectral composition analysis by EDX (spectrum 1) shows sodium and chlorine oxygen, which are clearly corrosion products. (Table 2)

Table 2. The spectral composition of the SLS sample.

Spectrum	O	Na	Si	Cl	Cr	Co	Mo	Total
Spectrum 1	24.53	1.19	1.12	0.59	28.76	34.30	9.52	100.00

3. Conclusions

In conclusion, the CAD/CAM milling sample proved to be the best in terms of structure and corrosion resistance, the worst being the SLS sample. The structure and corrosion behavior of CoCr alloys

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highly depends on the manufacturing process. In case of milling the alloy is in a bulk form, with a compact structure, with no noticeable impurities. No heating/sintering is involved in the manufacturing process, which might alter the alloy's properties. In case of CAD/CAM sintering, corrosion problems may occur due to the presence of the binder and because of the final sintering stage. In case of SLS, the powder nature of the alloy and the manufacturing process may cause corrosion. 3D Printing is constantly developing, so CoCr alloys manufactured using these technology will probably become serious competitors for prosthetic dental applications. The low price and the ease of execution using virtual impressions and design are some of the advantages. Traditional casting may be successfully replaced by 3D Printing and CAD/CAM milling, which represent a logical step towards the future.

4. References

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