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Corrosion behavior of dental CoCr alloys made by different digital workflow processes compared to cast CoCr alloys

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Abstract – Dental metallic restorations can be made alternatively by casting or CAD/CAM procedures such as milling and selective laser melting. This raises the question as to how far the material properties differ. The aim of this study was to evaluate the corrosion behavior of dental porcelain fused CoCr alloys manufactured by the CAD/CAM techniques using wet milling of solid blanks (Organic), dry milling of 'wax-like' blanks and subsequent sintering (Ceramill Sinron) and selective laser melting (Remanium Star CL) compared to the cast CoCr alloys Remanium Star, Girobond NB and Ankatit U. Corrosion measurements according to ISO 10271 were performed with all alloys. Static immersion tests over 1, 4 and 7 days were used in artificial saliva. The electrolytes of all samples were analyzed by ICP-OES and the corresponding ion release rate was calculated for each alloy and immersion time. Furthermore, electrochemical corrosion measurements were carried out in 0.9% saline. Open-circuit-potential measurement over 2 h were carried out, followed by anodic polarization from -150 mV ~Ecorr to 1 V at a speed of 1 mV/sec. The results revealed a total ion release below 50 µg/cm² for all alloys investigated which is below the limit value of 200 µg/cm² according to ISO 22674.

Keywords – dental CoCr alloys, static immersion test, electrochemical corrosion, digital workflow

1. INTRODUCTION

Traditionally metallic dental restorations are cast. Since a few years metallic dental restorations can be made alternatively by CAD/CAM procedures using various technologies such as milling or selective laser melting. If a new dental alloy comes onto the market it must fulfill the requirements according to ISO 10271 and ISO 22674 [1, 2] in order to get CE certificate. Based on the different conditions in mouth (e.g. pH change, fluoride applications) a dental alloy must have a good corrosion resistance and biocompatibility. Corrosion studies which compared dental CoCr alloys made by casting and laser melting procedure, have demonstrated a very low Co release rate in static immersion tests for both state [4-7].

Aim of the study: The aim of this study was to evaluate the corrosion behavior of dental porcelain fused CoCr alloys manufactured by the CAD/CAM techniques wet milling of solid blanks (Organic), dry milling of 'wax-like' blanks and subsequent sintering (Ceramill Sintron) and, selective laser melting (Remanium Star CL) compared to the cast CoCr alloys Remanium Star, Girobond NB and Ankatit U. The hypotheses of the study were:

- First working hypothesis: The method of preparation of CoCr alloys does not affect the ion release rate using the immersion test.
- Second working hypothesis: The electrochemical corrosion behavior of CoCr alloys is not influenced by kind of preparation.

2. MATERIAL AND METHODS

Materials

In Tab. 1 the composition of all CoCr alloys used in this study can be seen.

TABLE I
COMPOSITION IN MASS PERCENT [M/M] OF THE CO-CR ALLOYS USED IN THIS STUDY AND PRE VALUES

Element	Remanium Star	Organic CoCr	Ceramill Sintron	Girobond NB	Ankatit U
Co	61.0	63.55	66.0	62.0	62.30
Cr	28.0	28.40	28.0	25.0	25.20
Mo	-	6.0	5.0	5.0	6.0
W	9.0	-	-	5.0	5.0
Fe	-	0.5	< 1	< 1	-
Nb	x	0.5	-	< 1	-
Si	1.5	0.7	< 1	1.2	-
Mn	-	0.6	< 1	-	-
Ce	-	-	-	0.3	-
N	x	-	-	< 1	-
Ni	-	0.05	-	-	-
C	-	0.002	-	-	< 0.02
PRE	42.85	48.20	44.50	49.75	53.25

The PRE value (pitting resistance equivalent) is a number which express the pitting corrosion resistance for a metal based on its chemical composition. For dental alloys the PRE must be more than 35 [3]. The PRE value was calculated according to equation 1:

$$PRE = Cr + 3.3(Mo + W) \quad (1)$$

In Table II the alloys investigated and different working procedures are listed.

TABLE II
OVERVIEW OF THE WORKING PROCESS OF EACH COCR ALLOY

Manufacturer	Alloy name	LOT No	Working process
Dentaurum	Remanium Star cast	548	Dental casting
Dentaurum	Remanium Star CL	25686 /#407703	Selective laser melting
Rübeling & Klar	Organic CoCr	13/3151	CAD/CAM Milling
Amann Girrbach	Ceramill Sintron	12D051	CAD/CAM and sintering
Amann Girrbach	Girobond NB	11-607	Dental casting
Anka-Guß	Ankatit U	2259	Dental casting

Sample preparation

From each alloy 6 samples with a size of 30×10×1.5 mm³ for static immersion test and 4 round samples (10 mm diameter, thickness 1.5 mm) for electrochemical corrosion measurements were prepared according to ISO 10271. All samples were wet ground with SiC 1200 abrasive paper (Metaserv, Bühler-Wirtz, Düsseldorf). Since all alloys are ceramic alloys, a simulated porcelain firing was done with all samples. For Remanium Star, Organic CoCr and Ankatit U were put into a furnace (Vacumat 500, Vita, Bad Saeckingen) and the following firing schedule was used: Starting temperature: 600 °C, heating rate 7 minutes to the end temperature of 950°C which was held to 10 minutes. The firing schedule for Ceramill Sintron and Girobond NB which was repeated 6 times can be seen in Table 3.

TABLE III
FIRING SCHEDULE FOR CERAMILL SINTRON AND GIROBOND NB

	Oxide firing	1st Opaque	2nd Opaque	1st Dentin	2nd Dentin
Start temperature [°C]	550	550	550	580	580
Closing Time [min.]	-	6	6	6	4
Heating rate [°C/min]	80	80	80	55	55
Vacuum	-	+	+	+	+
End temperature [°C]	1000	1000	950	920	910
Holding time [min.]	1	1	1	1	1

After the firing each sample was ground again with SiC 1200 to remove the oxide layer in compliance with ISO 10271.

For electrochemical corrosion testing a CoCr wire was laser welded on the back side of each sample and isolated with a shrinkage tube. All samples were embedded in Palavit and ground again with SiC 1200 grit.

Static immersion test

After grinding the surface area of each sample was determined using a digital caliper. Each sample was ultrasonically cleaned in ethanol for five minutes, brought into a plastic tube and filled with 10 ml of artificial saliva which consisted of 0.1 M sodium chloride and 0.1 M lactic acid (pH 2.3). All samples were stored in a heating chamber at 37°C. After 1, 3 and 3 days the electrolytes were analyzed by ICP-OES (Optima 4300 DV, Perkin Elmer) and replaced by fresh ones.

Electrochemical corrosion measurements

With all alloys electrochemical corrosion measurements according to ISO 10271 were performed. After ultrasonically cleaning each sample was brought into an electrochemical cell which was filled with 0.9 % saline and heated at 37°C. With each sample open-circuit-potential was measured over 2 hours followed by anodic polarization from -150 mV~Ecorr until 1 V (Ref) at a speed of 1 mV/sec. From each measurement the parameters Ecorr after 2 h, the zero potential Ez, the breakdown potential Ep and corresponding ip, the corrosion current density icorr and the current density at 300 mV + Ez were calculated.

Statistics

The ion release of Co from static immersion test and the calculated electrochemical corrosion parameters were statistically evaluated by independent Student's t-Test ($p < 0.05$) using Origin 8.5.

3. RESULTS

Static immersion test

In Figure 1 the Co release of each alloy tested is presented depending on immersion time. For all alloys the Co release is very low with values below 10 µg/cm².

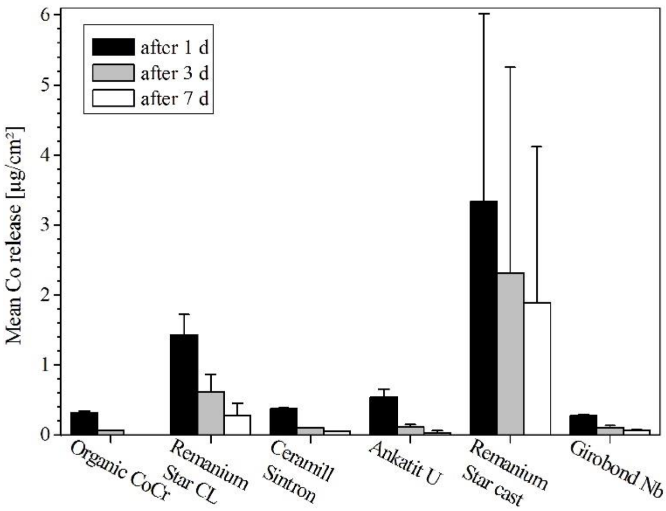

FIGURE 1
MEAN CO-RELEASE AND STANDARD DEVIATION AFTER 1, 4 AND 7 DAYS IMMERSION TIME.

The calculated mean Co release rate per day after 1, 4 and 7 days which can be seen in Figure 2, showed that after 7 days of immersion the Co release rate decreased to almost zero for all alloys tested.

Remanium Star cast showed the highest Co release rate for each immersion time ranging from 3.5 to 1.5 µg/(cm²×d). All other alloys showed a similar Co release rate with values below 1 µg/(cm²×d) with decreasing trend.

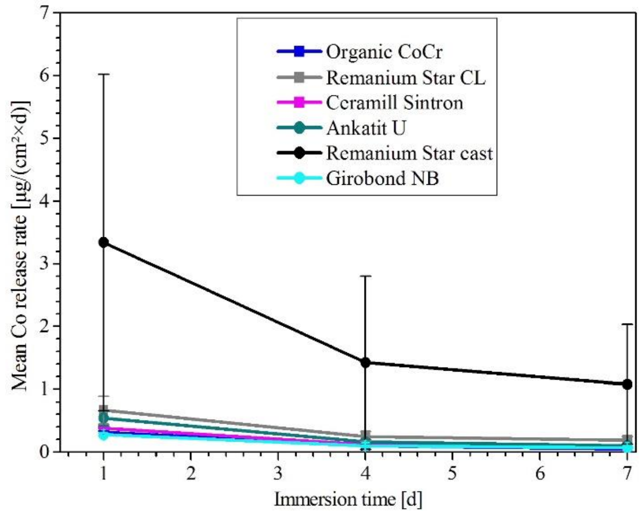

FIGURE 2
CALCULATED MEAN CO RELEASE RATE AFTER 1, 4 AND 7 DAYS.

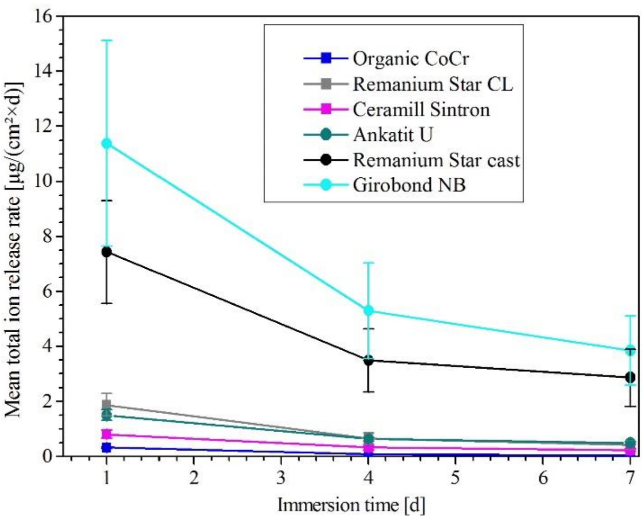

FIGURE 3
CALCULATED MEAN TOTAL ION RELEASE RATE AFTER 1, 4 AND 7 DAYS.

In Figure 3 the mean total ion release rate is presented. This diagram is similar to that of Figure 2, but the values are higher for Remanium Star cast and Girobond NB. The cause for that can be seen in Figure 4 which show the ranking of element release for each alloy tested.

The mean total ion release of each alloy depending on immersion time which is presented in Figure 4 showed that from all alloys tested Organic CoCr has the lowest total ion release with values below 1 µg/cm² which consists only of the Co solubility. The total ion release with < 3 µg/cm² was on a similar low level for Ceramill Sintron and Ankatit U. Girobond NB showed the highest total ion release > 25 µg/cm² of all alloys tested which is mainly caused by the release of Ce. Remanium Star cast showed a higher mean total ion-release compared to the selective laser melted one. In both manufacturing procedures the Co release was dominant.

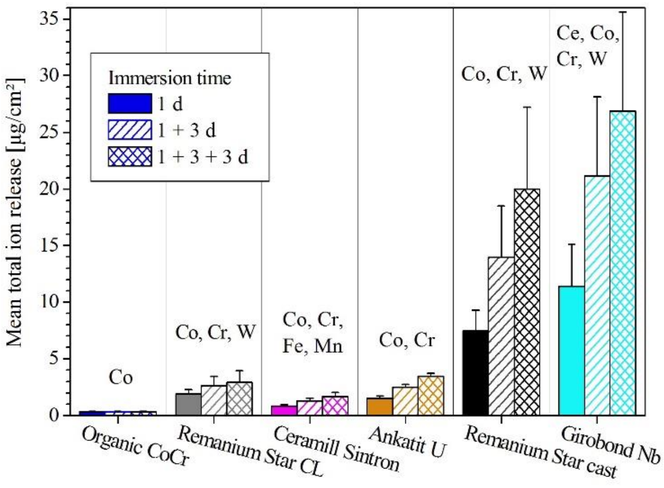

FIGURE 4
MEAN TOTAL ION-RELEASE OF EACH ALLOY TESTED DEPENDING ON IMMERSION TIME. THE SOLUBILITY OF THE FOUND ELEMENTS IS SORTED ACCORDING TO THEIR QUANTITY.

Electrochemical corrosion

The results of all electrochemical corrosion measurements can be seen in Figure 5 and 6, respectively and Table 4 and 5.

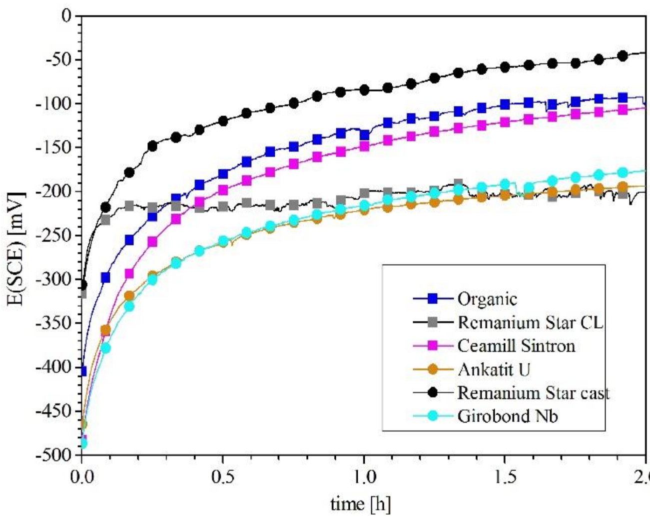

FIGURE 5
OPEN-CIRCUIT-POTENTIAL MEAN CURVES OVER 2 H FOR EACH ALLOY TESTED.

The results represented in both figures show a similar electrochemical corrosion behavior for Organic CoCr and Ceramill Sintron. For these two alloys the Ecorr values after 2 h range between the Ecorr value of Remanium Star cast, Ankatit U, Girobond NB and Remanium Star CL. For the last three alloys the Ecorr values had the most negative potentials which are in a similar order. The effect of the manufacturing procedure can be seen with Remanium Star: The cast one showed a steady increase of the potential from beginning to end. However, the laser melted one showed only a small increase of potential in the first 10 minutes, holding this potential until end. These two alloys showed the highest potential difference after 2 h (-42 mV with Remanium Star cast and -200 mV with Remanium Star CL). For the anodic polarization measurements, this difference can be seen with the parameter ip which is in contrast lower for the cast one compared to the laser melted one. The laser melted alloy showed a similar electrochemical corrosion behavior with

Ankatit U which showed the highest ip values of the alloys tested. These two alloys represent the lowest and highest PRE value of all alloys tested here. In this case no correlation of the PRE value with corrosion data could be found.

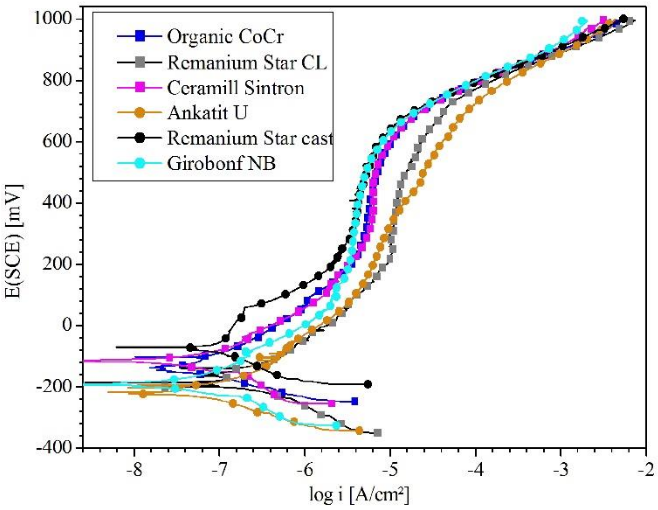

FIGURE 6
MEAN ANODIC POLARIZATION CURVES OVER 2 H FOR EACH ALLOY TESTED.

TABLE IV
CALCULATED PARAMETERS FOR THE CO-CR ALLOYS MADE BY DIGITAL WORKFLOW

Parameter	CoCr alloys made by CAD/CAM		
	Organic CoCr	Remanium Star CL	Ceramill Sintron
Ecorr after 2 h [mV]	-98 ± 36	-200 ± 24	-104 ± 24
Ez [mV]	-137 ± 40	-167 ± 51	-114 ± 26
Ep [mV]	668 ± 34	706 ± 40	656 ± 10
ip [µA/cm²]	11 ± 6	16 ± 10	7 ± 1
icorr [nA/cm²]	59 ± 14	183 ± 78	96 ± 10
i(300 mV+Ez) [µA/cm²]	3 ± 0	1 ± 1	3 ± 1

TABLE V
CALCULATED PARAMETERS FOR THE CAST CO-CR ALLOYS

Parameter	Cast CoCr alloys		
	Ankatit U	Remanium Star cast	Girobond NB
Ecorr after 2 h [mV]	-194 ± 38	-42 ± 66	-176 ± 17
Ez [mV]	-215 ± 37	-37 ± 18	-189 ± 18
Ep [mV]	708 ± 27	685 ± 57	650 ± 7
ip [µA/cm²]	31 ± 17	7 ± 8	6 ± 1
icorr [nA/cm²]	87 ± 3	106 ± 87	65 ± 8
i(300 mV+Ez) [µA/cm²]	3 ± 0	2 ± 0	2 ± 0

4. CONCLUSIONS

Based on this study the following conclusions can be drawn:

• The results from static immersion tests showed that the Co release rates were very low (nearly to zero) for all alloys tested. With these results the first working hypothesis can be confirmed.

• Based on the limit value of total ion release of 200 µg/cm² given in ISO 22674 all alloys tested in this study fulfill this requirement with ion release values below 50 µg/cm².

• A ranking / evaluation of the alloys tested can be done but the ranking strongly depends on the used measurement method and parameter:

- The milled CoCr alloy Organic CoCr showed the lowest total ion-release and lowest icorr value of all alloys tested.
- Remanium Star cast showed a higher total ion release compared to the laser melted one. In contrast, the electrochemical corrosion resistance was better for the cast one compared to the laser melted alloy. Both manufacturing procedures showed icorr values > 100 nA/cm² compared to all other alloys tested (< 100 nA/cm²).
- The CoCr sinter alloy Ceramill Sintron is superior compared to Remanium Star laser melted alloy (total ion release and icorr). Compared to the milled CoCr alloy Organic CoCr the corrosion behavior is similar.

• Concerning the PRE value used here, no correlation can be found for both, immersion test as well as electrochemical corrosion test data.

Based on this study it could be shown that the cast alloy had a good corrosion resistance in general. The improvement of the corrosion resistance for the CoCr alloys made by digital workflow were low but can be seen with both corrosion measurement types especially for the milled Organic CoCr and the sinter alloy Ceramill Sintron.

Acknowledgment

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5. REFERENCES

[1] ISO 10271 (2011): Dentistry – Corrosion test methods for metallic materials.

[2] ISO 22674(2016): Dentistry–Metallic materials for fixed and removable restorations and appliances.

[3] Al Jabbari, YS, "Physico-mechanical properties and prothodontic applications of Co-Cr dental alloys: a review of the literature", *J Adv Prosthodont*, 6, 2014, 38-45.

[4] Al Jabbari, Y, Koutsoukis, T, Barmpagadaki, X, Zinelis, S, "Metallurgical and interfacial charcterization of PFM Co-Cr dental alloys fabri-cated via casting, milling or selective laser melting", *Dent Mater*, 30, 2014, e79-e88.

[5] Xin, Y-Z Chen, J, Xiang, N, Gong, Y, Wie, B, "Surface characteristics and corrosion properties of selective laser melted Co-Cr dental alloy after porcelain firing", *Dent Mater* 30, 2014, 263-270.

[6] Suleiman, SH, Vult von Steyern, P, "Fracture strength of porcelain fused to metal crowns made of cast, milled or laser-sintered cobalt-chromium", *Acta Odont Scand*, 71, 201, 1280-1289.

[7] Qiu, J, Yu, W-Q, Zhang, F-Q, "Effects of the porcelain-fused-to-metal firing process on the surface and corrosion of two Co-Cr dental alloys", *J Mater Sci*, 46, 2011, 1359-1368.