# Assessment of mechanical properties and microstructure of Co-Cr dental alloys manufactured by casting, milling, and 3D printing

by

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A Thesis submitted to the Faculty of Graduate Studies of The University of Manitoba

in partial fulfillment of the requirements of the degree of

**MASTER OF DENTISTRY**

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## ABSTRACT

### Purpose

The aim of the present study is to investigate the effect of the three different Co-Cr manufacturing processes on the mechanical properties and microstructure of Co-Cr dental alloys.

### Methods

Dumbbell-shaped specimens (n=6) were fabricated with CAST (lost wax casting technique), CNC (computer numerical control milling), and DMLS (direct metal laser sintering) techniques. The mechanical propertied were evaluated following the (ISO) standard 6892. Tensile test was performed to evaluate 0.2% yield strength, tensile strength, elongation, and elastic modulus, 3-point-bending test was done for flexural strength, and microhardness test to analyze hardness. The microstructure was evaluated through scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDX), as well as X-ray diffraction analysis (XRD) for alloy phase identification. Statistical differences for the tensile test, 3-point-bending, and hardness were evaluated by one-way ANOVA followed by post hoc Tukey tests to determine the interaction among the groups.

### Results

The DMLS groups showed the highest values for 0.2% yield strength (908.0±13.1MPa), tensile strength (1123.7±6.5MPa), flexural strength (2273.0±43.2MPa), and microhardness (438.2±44.9HV) followed by CAST (462.1±8.0MPa, 632.6±23.7MPa, 1351.2±35.7MPa, and 400.0±33.3HV respectively) and CNC (413.0±10.0MPa, 533.1±17.4MPa, 1155.6±41.7MPa, and 295.0±22.1 HV respectively). No statistical differences found for elongation between CNC (15.3±3.9%) and DMLS (10.1±0.6%), as well as for DMLS (10.1±0.6%) and CAST (2.3±0.2%) (P>.05). No statistical differences found for elastic modulus among all groups (P>.05). EDX

revealed a slightly different chemical composition among the groups. XRD spectra revealed face-centered cubic (fcc) as the dominant phase and a small amount of hexagonal close-packed (hcp) in all three tested groups, as well as a peak of σ phase identified exclusively in the CAST group.

## Conclusions

The mechanical properties and microstructures of Co-Cr dental alloys is dependent on the fabrication method. Overall, DLMS specimens performed better than CAST and CNC.

## Acknowledgements

I’d like to start by thanking my research committee, Dr Igor Pesun, Dr Rodrigo Franca, and Dr Charlene Salomon for their support and guidance throughout this process. I appreciate the teachings provided throughout my residency and the mentorship that have made my academic years at the University of Manitoba memorable.

Thank you to Cross-town dental lab and 3DRPD for their support in providing the samples for this research. And a special recognition must be made to the American Academy of Fixed Prosthodontics (AAFP) for enabling the funding for this research through the Tylman Research Award.

## Dedication

This thesis is dedicated to my husband Leo and my family in Brazil for all their encouragement and support throughout this entire process always pushing me to be the best version of myself. To my co-resident Paul Mikhail for encouraging me to be a better person and clinician. And to God for allowing me to experience great things in life.

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# CHAPTER 1

## Introduction

## Literature review

### 1. Use of Cobalt-Chromium in dentistry

Cobalt-Chromium alloys have been used in dentistry since the 1930s for the fabrication of removable partial denture frameworks. The most popular metals at that time were Co-Cr, Nickel-Chromium (Ni-Cr), and Type IV gold alloys. Co-Cr alloys have a major advantage over Type IV gold alloys as their density is almost half of the gold-based alloys which allows it to produce a significantly lighter framework.(Al Jabbari, 2014) With the increasing cost of noble alloys, Co-Cr became the most commonly used base-metal alloy in dentistry since the 1980s as they were a relatively inexpensive replacement for noble alloys (Revilla-León et al., 2021; Sulaiman, 2020) and the most common alternative for use in individuals with nickel allergy.(Revilla-León et al., 2021; Xing et al., 2022) Known for its mechanical properties and biocompatibility (Craig & Hanks, 1988), the applicability of Co-Cr alloys ranges from fixed to removable prosthodontics.

The literature describes Co-Cr alloys as being biocompatible, heat resistant, non-magnetic, with favorable resistance to wear, tarnish, and corrosion. (Evans & Thomas, 1986; Viennot et al., 2005) In recent years, different methods of fabrication have been introduced to overcome the flaws of the conventional method and to increase predictability and efficiency for dental framework production. Nowadays, Co-Cr has been used mainly for the fabrication of removable partial denture frameworks, as well as a replacement for Ni-Cr alloys for the fabrication of porcelain fused to metal (PFM) restorations.

## 2. Lost-wax casting technique

The lost wax casting (LWC) technique has been in use since 1907 and has been the primary method of fabricating metal restorations in dentistry ever since. Because of its low cost and popularity, LWC is still a common fabrication method for metal structures in the dental industry.(Myszka & Skrodzki, 2016; M. Wu et al., 2022) This method is, however, progressively losing its popularity due to being time consuming, technique sensitive,(Kim et al., 2014) and hard to manipulate in the dental laboratory due to the high melting temperature of Co-Cr alloys.(Kim et al., 2016; Wataha & Messer, 2004) This conventional fabrication method has unavoidable distortion of the wax pattern and inherent structural defects caused by the melting and cooling characteristics of the alloy.(Wataha & Messer, 2004)

## 3. Computer-aided design - computer-aided manufacturing (CAD-CAM) technique

Computer-aided design and computer-aided manufacturing (CAD-CAM) was introduced to the dental field in the early 1980s and has been shown to reduce flaws and porosities inherent from the conventional fabrication method.(Alhallak & Nankali, 2021; Han et al., 2018; Kim et al., 2016) This technology comprises two main categories: a subtractive manufacturing process (SM), and an additive manufacturing (AM) process.

### 3.1 Subtractive manufacturing process (SM)

The SM is a computer numerical control (CNC) milling process that grinds a block into the desired shape improving the precision of the framework (Bae et al., 2015) while reducing the manufacturing time. The CNC fabrication method utilized Co-Cr alloy blanks that are manufactured under highly standardizer industrial conditions which reduces significantly the flaws obtained by the melting and cooling rates of the CAST technique. One of the major advantages of

SM is the substantial reduction of porosity (Xing et al., 2022) of the final objects.(Koutsoukis et al., 2015) However, this process leads to a high waste of tools and materials (Yu et al., 2021) and presents a limitation in manufacturing complex objects due to the limited movement of their axis.(Lebon et al., 2016; Strub et al., 2006)

### 3.2 Additive manufacturing process (AM)

Additive manufacturing technology allows complex 3D objects to be fabricated in a short period of time (Sulaiman, 2020) with little or no porosity, (Wu et al., 2014; Xing et al., 2022) no residual stress due to the heat treatment applied,(Konieczny et al., 2020; Lee et al., 2022) high dimensional accuracy,(Alageel et al., 2018; Wu et al., 2014) and considerably less material waste than the SM process.(Strub et al., 2006) It has also been reported to provide higher patient satisfaction for the fabrication of partial frameworks when compared to conventional methods due to more precise fit of the framework.(Almufleh et al., 2018) Powder bed fusion (PBF) is the most commonly employed AM technology for metal processing in dentistry;(Alageel et al., 2018; Myszka & Skrodzki, 2016; Oliveira & Reis, 2019; Revilla-León & Özcan, 2017) it can be subdivided into three main methods: selective laser sintering (SLS), selective laser melting (SLM), and electron beam melting (EBM). Selective laser sintering uses laser energy to heat and fuse the metal powder into a thin solid layer (20-100 μm) (Revilla-León et al., 2020) without fully melting the metal powder,(Konieczny et al., 2020) while SLM and EBM fully melt the metal powder.(Myszka & Skrodzki, 2016; Revilla-León et al., 2021; Wu et al., 2022) The main difference between SLM and EBM is the energy source (laser or electron bean).(Revilla-León et al., 2021) Direct Metal Laser Sintering (DMLS) is also a variation of PBF that uses a mixture of metal powders with high and low melting temperatures.(Alageel et al., 2018) During the processing procedure the metal powder with low melting temperature fully melts while the high melting temperature powder only melts partially.(Ahn, 2016; Kruth et al., 2005) The major disadvantage of AM technology is the high manufacturing cost which restricts this method to few specific CAD/CAM centers in the dental industry.(Kim et al., 2016; Krug et al., 2014)

## Statement of Problem

Different authors reported that different manufacturing methods result in metal alloys with different microstructures (Al Jabbari et al., 2014; Kim et al., 2016; Revilla-León et al., 2021; Wu et al., 2022; Xing et al., 2022; Zhou et al., 2018) and mechanical properties.(Dolgov et al., 2016; Hong et al., 2020; Hong et al., 2022; Kim et al., 2016; Øilo et al., 2018; Okazaki et al., 2019; Wu et al., 2014; Yu et al., 2021; Zhou et al., 2018) However, the available data on the mechanical properties of Cobalt-Chromium alloy fabricated by SM and AM technologies used in dentistry is still limited.(Revilla-León et al., 2020; Revilla-León & Özcan, 2017; Sulaiman, 2020) With their increased use in the dental industry, it is crucial to have more understanding and information on the digital manufacturing processes.

## Purpose of the Study

The aim of this paper is to investigate the effect of the three different Co-Cr manufacturing processes on the mechanical properties and microstructure of Co-Cr dental alloys.

## Objectives of the study

- To measure the following mechanical properties: 0.2% yield strength, tensile strength, elongation, elastic modulus, flexural strength, and microhardness.

- To obtain a representation of the microstructure and element composition.

**Null hypothesis**

The null hypothesis is that there is no significant difference in the mechanical properties and microstructures resulting from different manufacturing processes.

# CHAPTER 2

## Materials and methods:

### Sample preparation

Three commercially available Co-Cr alloys were tested. The composition and manufacturer information are listed in Table 1. Dumbbell-shaped specimens were designed according to ISO 22674 (Figure 1) using a proprietary AutoCAD software. The design was converted into a standard tessellation language (.stl) format and used for the fabrication of the specimens according to each manufacturer's instruction.

**Table 1.** Brand name, manufacturer, and element composition of each material used per group.

| Group | Brand Name | Manufacturer | Element composition (wt%) as per manufacturer |
|---|---|---|---|
| CAST | Wironit | Bego, Quebec, Canada | Co: 63.0, Cr: 30.0, Mo:5.0, Si: 1.0, Mn: 1.0; C: <1.0 |
| CNC | Magnum Splendidum | MESA, Brescia, Italy | Co: 61.0, Cr: 28.0, W:8.5; Si: 1.5, Mn: <1.0, Fe: <1.0 |
| DMLS | Modelstar S Powder | Scheftner, Mainz, Germany | Co: 61.5, Cr: 28.5, Mo:6.0, Si: <1.0, Mn: <1.0, Fe: <1.0; C: <1.0 |

Key: CAST, lost wax casting technique; CNC, computer numerical control milling; DMLS, direct metal laser sintering; Co, Cobalt; Cr, chromium; Mo, molybdenum; Si, silica; Mn, manganese; Fe, iron; C, carbon; wt%, weight percentage.

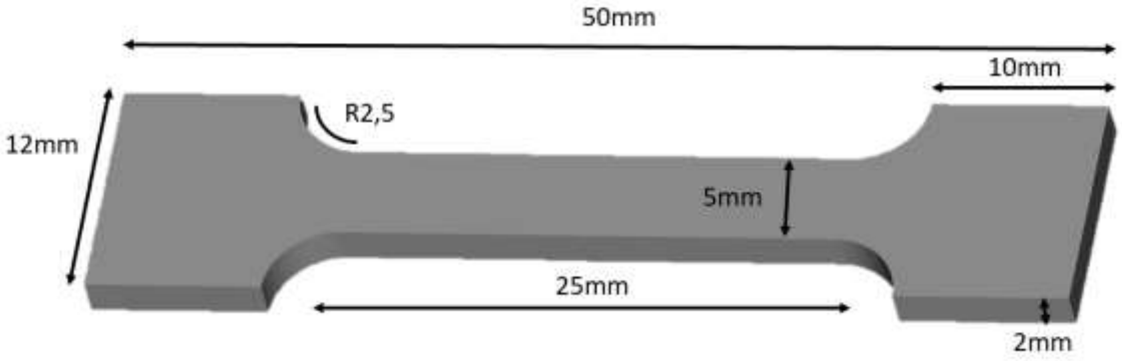

**Figure 1.** Specimen dimensions according to ISO 22674.

The CAST group specimens were fabricated by the lost-wax technique from a printed wax pattern. The .stl file was used to fabricate a wax pattern with the same exact dimensions as the other groups. Printed wax patterns were fabricated on a SLA printer (Form 3, Formlabs, Somerville, MA, USA) with a castable wax (Castable wax V1, Formlabs, Somerville, MA, USA), and invested (Wirovest, Bego, Quebec, QC, Canada) and casted using a Co-Cr ingot (Table 1) on a high-frequency centrifugal casting machine (Fornax T, Bego, Quebec, QC, Canada).

For the CNC group, specimens were milled using prefabricated Co-Cr alloy blanks (Table 1) on a 5-axis milling machine (Roders RXD5, Roders TEC, Germany). In the DMLS group, specimens were fabricated by transferring the .stl file to a high-performance 3D printer (ProX DMP 200 Dental, 3D Systems, Rock Hill, SC, USA) according to the settings recommended by the manufacturer and specimens were fabricated using cobalt-chromium alloy powder (Table 1).

**Tests:**

Tensile test (n=6 per group following ISO 22674 specifications) was carried out at room temperature for the measurement of 0.2% yield strength, tensile strength, elongation, and elastic modulus with a crosshead speed of 1.5mm/min using a Universal Testing Machine (UTM) (Landmark Servo-hydraulic Universal Test Machine Model 370.10, MTS Systems Corporation, Eden Prairie, MN, USA) with an attached extensometer (Miniature Axial Extensometers Model 3442MTS, Epsilon, Jackson, WY, USA). The gauge length of each specimen was accurately measured with a digital caliper (CD-6 ASX, Mitutoyo, Aurora, IL, USA) within the gauge length interval to 0.01mm. For the measurement of flexural strength, the UTM was used to perform a 3-point-bend test (n=6) at a crosshead speed of 1.5mm/min until failure.

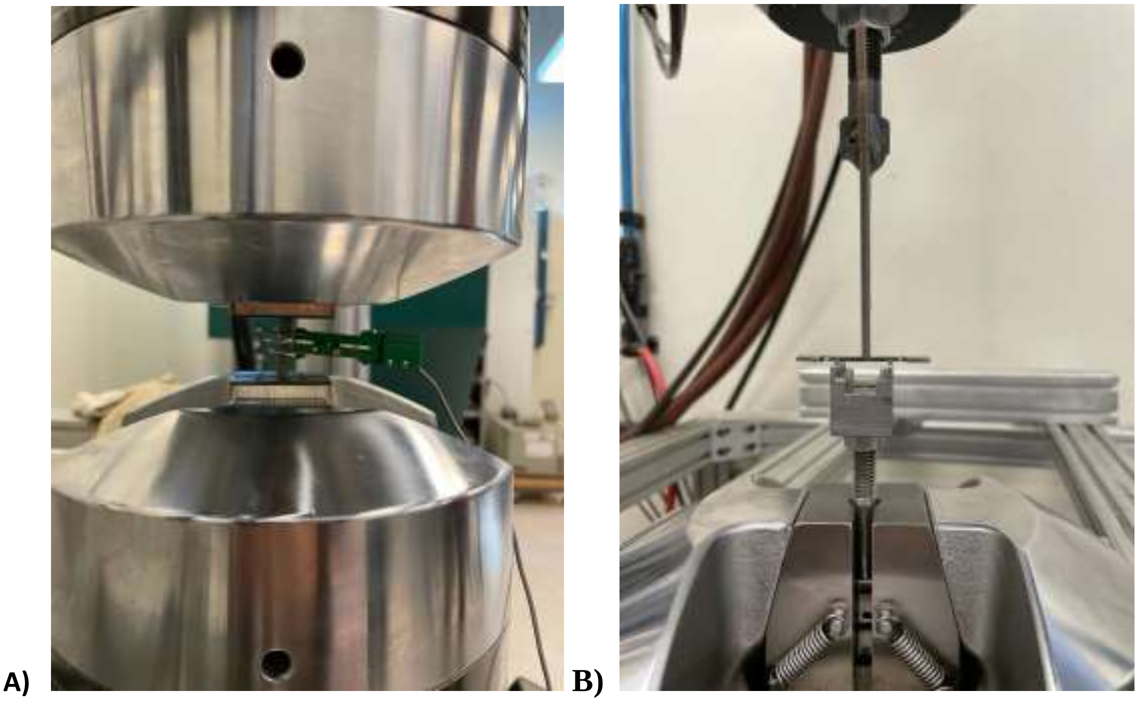

**Figure 2.** A) Tensile test, B) 3-point bending test.

For the microhardness test (n=6 per group following ISO 22674 specifications), the samples were mounted in phenolic resin (EasyFast, Struers Inc., Paris, France), ground with wet silicon carbide abrasive paper up to 2000 grit (LECO 8”, LECO, St. Joseph, MO, USA) and polished with 9µm, 6µm, and 3µm polycrystalline diamond suspension (MetaDi, Buehler, Lake Bluff, IL, USA). Microhardness was measured at 5 different spots on each specimen using a Vickers Hardness Tester (Micromet 5114, Buehler, Lake Bluff, IL, USA) with a load of 500gf and a dwell time of 20 seconds.

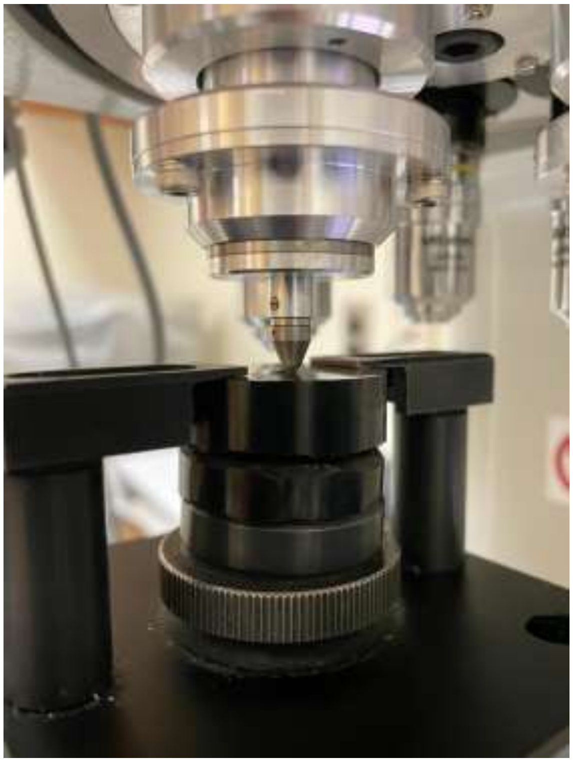

**Figure 3.** A) Microhardness test.

Following the microhardness test, specimens were etched for 30 seconds with hydrochloric acid/hydrogen peroxide (80:20 v/v) at room temperature. (Xing et al., 2022) Microstructure was analyzed (n=2 per group) by scanning electron microscopy (SEM) (FEI Nova NanoSEM 450, FEI, Hillsboro, OR, USA) under an accelerating voltage of 20kV and spot analysis was performed with energy dispersive X-ray analysis (EDX) in three different spots per specimen to determine the element composition of each tested specimen.

Phase identification was performed (n=2 per group) with an x-ray diffractometer (XRD) (Simens/Bruker D5000, Bruker, Aubrey, Texas, USA) equipped with a sealed X-ray tube. Samples were pre-scanned from 15-40° 2θ. Data was collected in two sample positions (0 and 90 degrees) with an accelerating voltage of 40kV, a beam current of 35mA, 2θ scan range between 35-100 degrees, and in step-scan mode using 0.02-degree step and 2 s dwell time.

## Statistical analysis

Statistical differences for the tensile test, 3-point-bending, and hardness were evaluated by one-way ANOVA followed by post hoc Tukey tests to determine the interaction among the groups. (Origin(Pro) 2023, OriginLab Corporation, MA, USA) Data was expressed as mean ±SEM. A *p* value of less than 0.05 was considered significant.

# CHAPTER 3

## Results

### 3.1 Mechanical properties

Mechanical properties and microstructure of three commonly used techniques of manufacturing Cobalt-Chromium alloy in dentistry were analyzed.

Through the tensile test, 0.2% yield strength, tensile strength, elongation, and elastic modulus were calculated for each group. As seen in Table 2, 0.2% yield strength and tensile strength were higher for the DMLS group (908.0±13.1 MPa and 1123.7±6.5 MPa) than those of CNC (413.0±10.0 MPa and 533.1±17.4 MPa) and CAST (462.1±8.0 MPa and 632.6±23.7 MPa). Statistically significant differences were found between the groups tested ($p < 0.05$). Elongation values were statistically different for the CNC (15.3±3.9 %) and CAST (2.3±0.2 %) with no statistical difference between DMLS (10.1±0.6 %) and the other two groups. No statistically significant differences were found between the groups in the overall average value for elastic modulus ($p > 0.05$). The 3-point bend test revealed the highest flexural strength for the DMLS group (2273.0±43.2 MPa), followed by CAST (1351.2±35.7 MPa) and CNC (1155.6±41.7 MPa). Statistically significant differences were found between the groups tested ($p < 0.05$).

The microhardness result values were highest for the DMLS (438.2±44.9 HV) group followed by CAST (400.0±33.3 HV) and lowest for CNC (295.0±22.1 HV) as seen in Table 2. Statistically significant differences were found between the tested groups ($p < 0.05$).

**Table 2.** Mean ± SEM mechanical properties and microhardness of CAST, CNC, and DMLS specimens.

| **Group** | **0.2% yield strength (MPa)** | **Tensile strength (MPa)** | **Elongation (%)** | **Elastic modulus (GPa)** | **Flexural strength (MPa)** | **Microhardness (HV)** |
|---|---|---|---|---|---|---|
| CAST | 462.1±8.0$^{B}$ | 632.6±23.7$^{B}$ | 2.3±0.2$^{B}$ | 209.1±20.0$^{A}$ | 1351.2±35.7$^{B}$ | 400.0±33.3$^{B}$ |
| CNC | 413.0±10.0$^{C}$ | 533.1±17.4$^{C}$ | 15.3±3.9$^{A}$ | 192.5±15.2$^{A}$ | 1155.6±41.7$^{C}$ | 295.0±22.1$^{C}$ |
| DMLS | 908.0±13.1$^{A}$ | 1123.7±6.5$^{A}$ | 10.1±0.6$^{AB}$ | 227.4±6.2$^{A}$ | 2273.0±43.2$^{A}$ | 438.2±44.9$^{A}$ |

Key: CAST, lost wax casting technique; CNC, computer numerical control milling; DMLS, direct metal laser sintering. SEM, standard error of mean.

Different letters represent significant differences (p <.05) between groups.

### 3.2 Microstructure

The representative SEM images of CAST, CNC, and DMLS are shown in Figure 4 in three different magnifications (x1000, x2000, x5000).

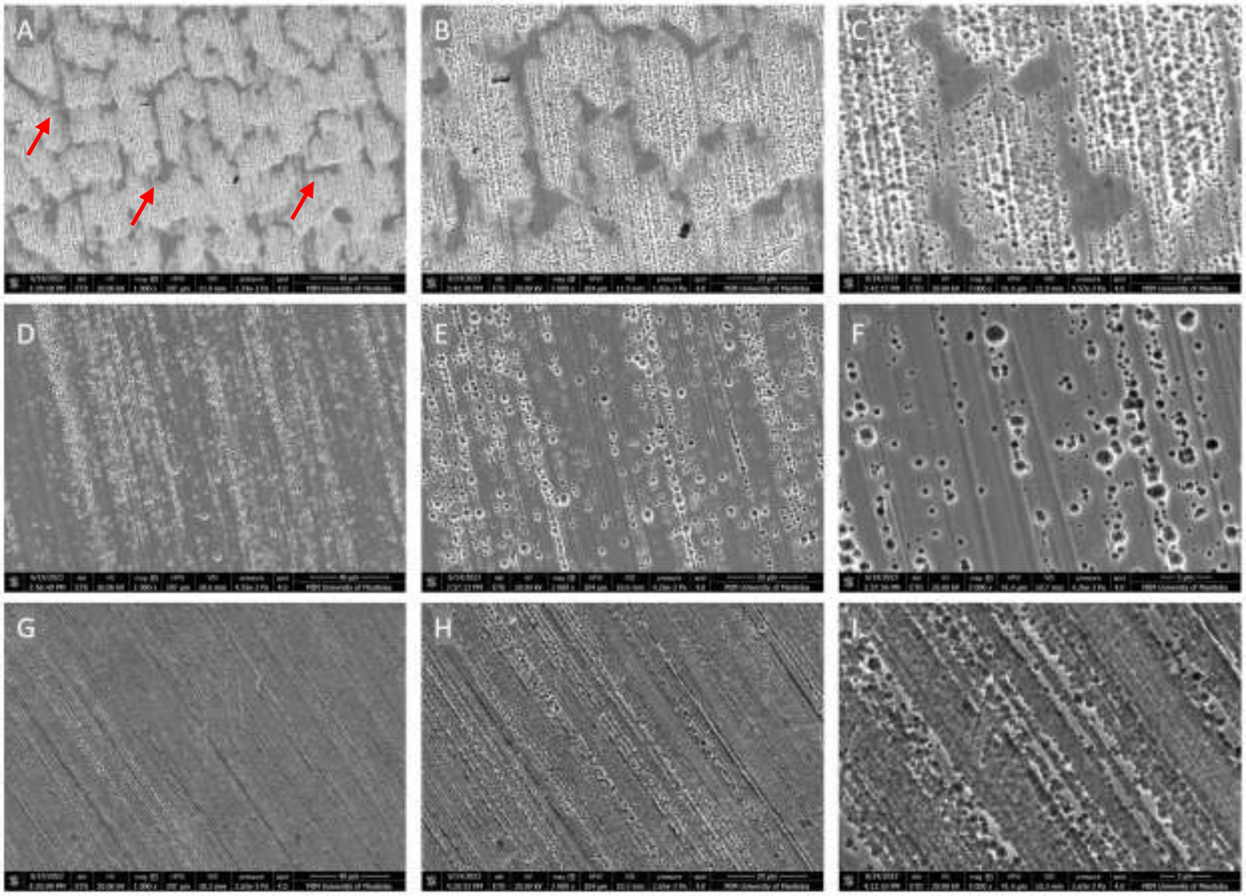

**Figure 4.** Representative scanning electron microscopy (SEM) of each tested group. A, B, C images are CAST; D, E, F images are CNC; G, H, I images are DMLS. Original magnification A, D, G, x1000. Original magnification B, E, H, x2000. Original magnification C, F, I, x5000.

Key: CAST, lost wax casting technique; CNC, computer numerical control milling; DMLS, direct metal laser sintering.

Table 3 illustrates the results of quantitative elemental spot analysis with EDX performed in 3 different spots on the same specimen. The greatest number of element types were found in the CNC group where tungsten (W) was found on an average of 7.0 wt% while no W was detected on CAST and DMLS. In addition, CNC presented the least percentage of Mo and Cr, CAST contained the highest percentage of Cr, and the greatest percentage of Co was found on the DMLS group. Co was the main element found in all teste alloys followed by Cr.

**Table 3.** Results of quantitative elemental spot analysis with Energy Dispersive X-ray analysis (EDX).

| | | **Element composition (wt%)** | | | | | |
|---|---|---|---|---|---|---|---|
| **Group** | **Spot** | **Co** | **Cr** | **Mo** | **Mn** | **Si** | **W** |
| CAST | 1 | 62.7 | 30.3 | 4.5 | 1.6 | 0.8 | ND |
| | 2 | 62.8 | 30.2 | 4.5 | 1.6 | 0.9 | ND |
| | 3 | 62.7 | 30.3 | 4.4 | 1.7 | 0.9 | ND |
| | **mean (SD)** | **62.7 (0.05)** | **30.2 (0.05)** | **4.4 (0.05)** | **1.6 (0.05)** | **0.86 (0.05)** | **ND** |
| CNC | 1 | 62.4 | 27.8 | 0.2 | 1.2 | 1.5 | 6.8 |
| | 2 | 62.1 | 27.7 | 0.2 | 1.3 | 1.6 | 7.1 |
| | 3 | 61.9 | 28.1 | ND | 1.4 | 1.5 | 7.1 |
| | **mean (SD)** | **62.1 (0.25)** | **27.8 (0.20)** | **0.2 (0)** | **1.3 (0.1)** | **1.5 (0.05)** | **7.0 (0.17)** |
| DMLS | 1 | 64.0 | 29.4 | 4.3 | 1.8 | 0.6 | ND |
| | 2 | 63.7 | 29.3 | 4.4 | 1.8 | 0.8 | ND |
| | 3 | 64.1 | 29.1 | 4.4 | 1.6 | 0.7 | ND |
| | **mean (SD)** | **63.9 (0.2)** | **29.2 (0.15)** | **4.3 (0.05)** | **1.7 (0.11)** | **0.7(0.1)** | **ND** |

Key: CAST, lost wax casting technique; CNC, computer numerical control milling; DMLS, direct metal laser sintering; Co, Cobalt; Cr, chromium; Mo, molybdenum; Mn, manganese; Si, silica; W, tungsten; wt%, weight percentage; ND, not detected.

The X-ray diffraction analysis (XRD) spectra of the three tested groups is displayed in Figure 5. In addition, Figure 6 shows the XRD pattern of the CAST 1 sample in an amplified scale to better illustrate the phases.

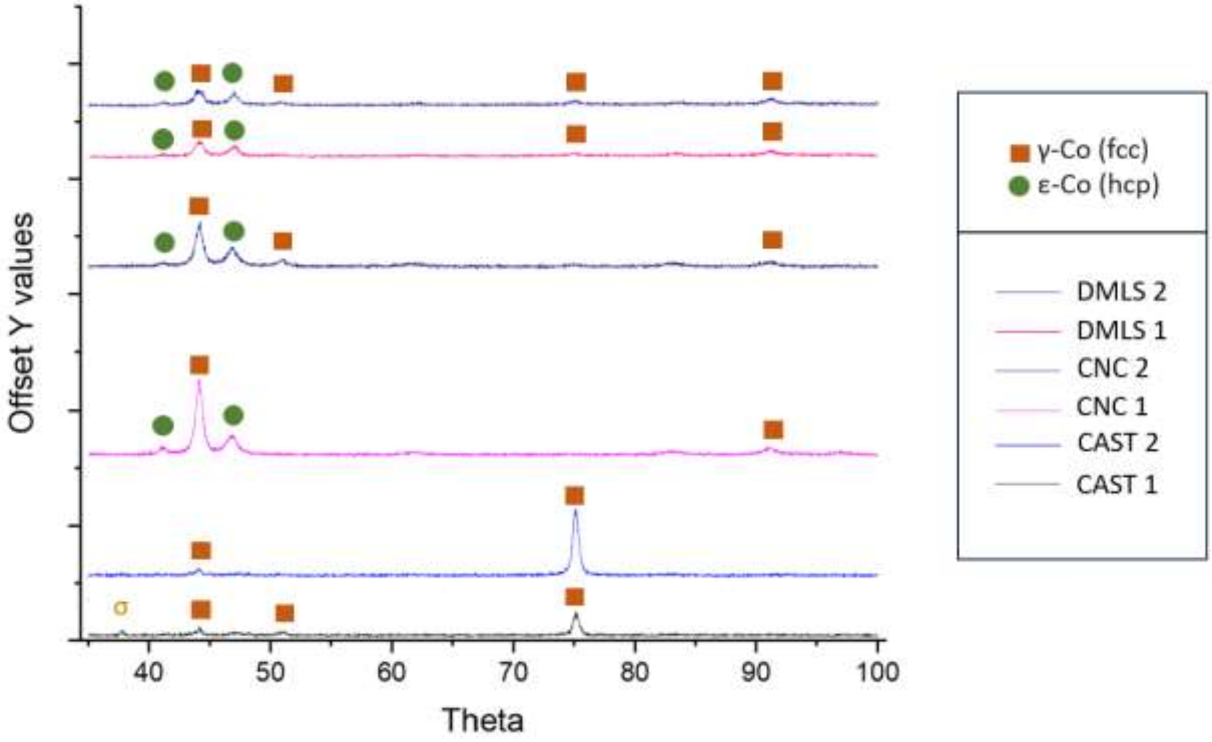

**Figure 5.** XRD spectra of the tested Co-Cr alloys.

Key: CAST, lost wax casting technique; CNC, computer numerical control milling; DMLS, direct metal laser sintering; XRD, X-ray diffraction. Fcc, face- center-cubic phase; hcp. Hexagonal closed-pack phase.

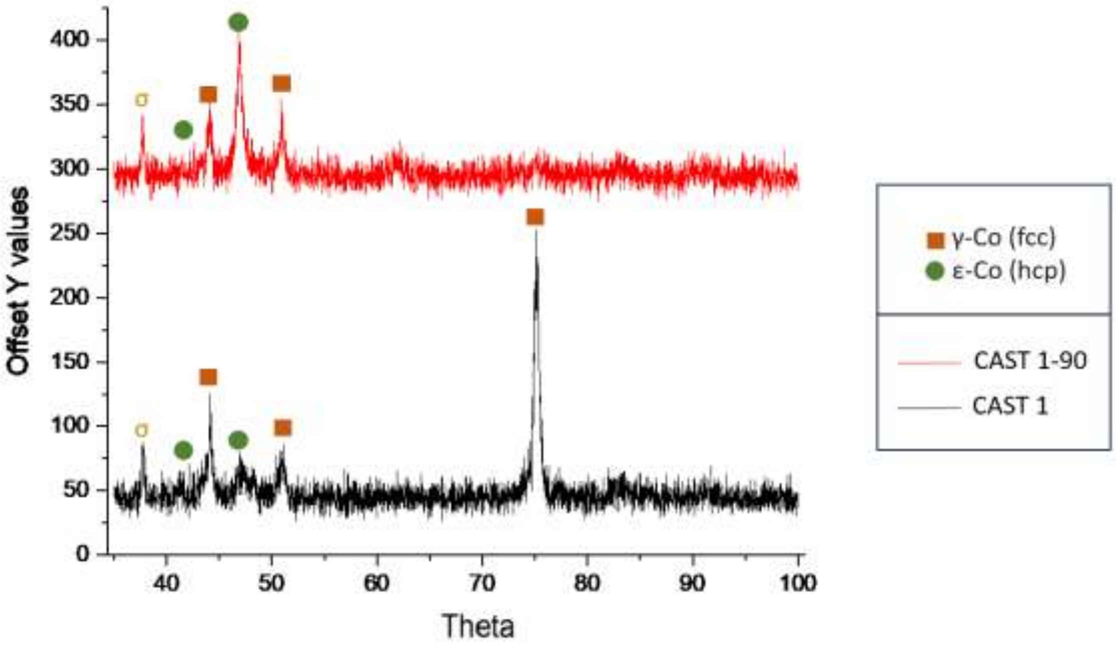

**Figure 6.** XRD spectra of CAST sample with 0- and 90- degree position.

Key: CAST, lost wax casting technique; XRD, X-ray diffraction. Fcc, face- center-cubic phase; hcp. Hexagonal closed-pack phase.

Face-centered cubic (fcc) and hexagonal close-packed (hcp) were the main phases of the Co-Cr alloy present in all three tested groups. The fcc phase was the dominant phase with a small amount of hcp. In addition, a peak of σ phase (intermetallic compound) was identified exclusively in the CAST group.

# CHAPTER 4

## Discussion

The present in vitro study investigated and compared the mechanical properties and microstructure of Co-Cr dental alloys fabricated by three different manufacturing methods (casting, additive, and subtractive manufacturing). In agreement with previous studies (Kim et al., 2016; Wang et al., 2016; Zhou et al., 2018) the present findings showed that the mechanical properties and microstructures of the tested alloys were dependent on the manufacturing method, thus the null hypothesis was rejected.

### 4.1 Mechanical properties

The ISO 22674:2016 classifies metallic materials that are suitable for the fabrication of dental restorations and appliances and specifies their mechanical requirements. Table 4 shows the mechanical properties required for Co-Cr and divides it into 5 types. All tested alloys satisfy the mechanical properties specified by the ISO 22674. The DMLS group is classified as type 5 (0.2% yield strength: >500 MPa; elongation: >2%; elastic modulus: >150 GPa) while CNC and CAST are classified as type 4 (due to 0.2% yield strength: <500 but >360MPa). According to the ISO 22674:2016 requirements, the tested alloys can be used for type 4 or 5 dental appliances (which include single crowns, thin veneered crowns, wide span bridges, removable partial dentures, and retention claps). For the proper design and selection of the alloy to be used for each clinical scenario, the clinical relevance of each mechanical property evaluated in this manuscript must be fully understood.

**Table 4.** Mechanical properties by type specified in ISO 22674.

| Type | 0.2% yield strength (MPa) | Elongation (%) | Elastic Modulus (GPa) |
|---|---|---|---|
| 0 | - | - | - |
| 1 | 80 | 18 | - |
| 2 | 180 | 10 | - |
| 3 | 270 | 5 | - |
| 4 | 360 | 2 | - |
| 5 | 500 | 2 | 150 |

Overall, Co-Cr dental alloy fabricated with DMLS presented statistically significant higher mechanical properties than CAST and CNC (Table 2).

A high 0.2% yield strength indicate a high resistance to plastic deformation which has a fundamental clinical application as permanent deformation on certain structures such as removable partial denture (RPD) rest seat and frameworks as well as fixed partial denture (FPD) frameworks could lead to prosthetic failure. All tested alloys have enough yield strength to withstand permanent deformation (more than 300 MPa), although the high 0.2% yield strength of the DMLS group allows the design of a thinner cross-section without compromising rigidity (Al Jabbari, 2014) and a slower loosening of clasp retention due to insertion and removal of a RPD framework as plastic deformation requires a higher stress load when compared to the other tested groups. (Kim et al., 2016) Another important application of this mechanical property is for metal-ceramic restorations, in the presence of plastic deformation, porcelain debonding will likely occur.

High tensile strength as well as high flexural strength are desirable properties as this provides higher fracture resistance and reduced risk for deformation. Opting for a stronger material decreases the chances of fracture of the metal structure and increases longevity of the prosthetic component. The present study included a tensile test to investigate fundamental mechanical properties, and a 3-point-bending test to evaluate the flexural strength of the alloys. Differently than the tensile forces, bending forces are complex in nature and must be investigated to facilitate the decision when choosing the appropriate dental alloy for each clinical situation as it represents the clinical scenario (oral function) more appropriately than the tensile forces. The DLMS group presented significantly higher tensile and flexural forces when compared to CNC and CAST. In accordance with the results of this study, higher strength values for AM alloys have been attributed to the differences in chemical composition and processing parameters.(Wu et al., 2022) From a clinical perspective, the advantages of opting for a high strength alloy include the possibility of fabrication a thinner structure, improving esthetics and preserving tooth structure. To that point, based on the results of the present study, the DMLS alloy would provide a better outcome.

Elongation is the amount of plastic deformation that occurs before fracture and is related to the workability of the alloy. As shown in the results, CNC had the highest values although not statistically different than DMLS. This behaviour can be explained by the presence of a higher amount of face-centered cubic (fcc) phase of the DLMS and CNC groups when compared to the CAST group (more details to be discussed in the microstructure chapter). On a clinical scenario, ductile alloys are beneficial for removable partial denture retention clasps as it allows adjustment of the retentive tip with less risk of fracture. The present results suggest that all tested alloys provide adequate ductility with CNC and DMLS offering statistically similar adjustability, while

CAST has a more brittle behaviour and consequently more prone to fracture when subject to stress (although DMLS and CAST did not present statistically different results). The literature suggests that for AM alloys, the elongation is highly dependent on the building direction (Takaichi et al., 2013; Yu et al., 2021). The results of this study satisfy the ISO standard for elongation; however, the building direction of AM Co-Cr alloys must be taken under consideration when a desirable elongation is required.

In comparison to other alloys such as Type IV gold (90GPa), Cr-Cr alloys present the higher elastic modulus resulting in increased rigidity which allows it to be designed in thinner cross sections without increased risk of fracture. All tested methods of fabrication generated similar elastic modulus showing that no benefits of one over another was reported for this mechanical property.

The DMLS alloy displayed the highest values for hardness suggesting that out of the tested alloys this is the best option to resist permanent distortion and scratching. The high hardness values of DLMS can be attributed to the sintering process which has been previously reported to reduce porosity (Al Jabbari et al., 2014; Wu et al., 2014) and provide a more refined grain structure (Wu et al., 2022) due to the residual stresses generated.  In contrast, CNC presented almost half of DMLS hardness which could be explained by the chemical composition (presence of W instead of Mo) of the alloys to be discussed in the microstructure section.

Previous literature has shown that, in comparison to CNC and CAST samples, AM samples present a finer grain structure. (Wu et al., 2022; Zhou et al., 2018) The more homogeneous surface as seen in Figure 4 as well as the improved grain refinement of AM samples explain the enhancement in ductility and toughness, which is the main reason for improved mechanical performance of DMLS samples. The mechanical results of the present study are in accordance with other in vitro studies (Kim et al., 2016; Wu et al., 2022) that also reported overall higher mechanical properties for the AM group.

Despite the promising mechanical properties of the DMLS group found in the present study, it has been suggested that mechanical properties can be affected by other factors such as building direction, metal particle size, and melting speed of the laser (Aboulkhair et al., 2019) and therefore results should be interpreted with caution. Other important factors such as resistance to corrosion and tarnish, metal-ceramic bonding, biocompatibility, and fit must also be further investigated so the newer technologies can safely, and predictability replace the traditional casting technique.

## 4.2 Microstructure analysis

The results of this study show that the microstructure of the tested alloys is depended on the method of fabrication, thus rejecting the null hypothesis that microstructure would be similar for the different fabrication methods.

### 4.2.1 Scanning electron microscopy (SEM)

Figure 4 shows a representation of SEM images of the Co-Cr specimens. Even though the etching protocol used for this test did not allow for the clear identification of the grain boundaries, the images obtained revealed a different microstructure pattern between the groups indicating that the three tested manufacturing methods affected the specimens' microstructures. The SEM images obtained imply a different thermomechanical behavior among the tested groups. The CAST specimens showed a typical dendritic structure (Fig 4 A – red arrow) characteristic of the slow cooling and solidification rates. The DMLS and CNC revealed a more homogeneous surface which is explained by the rapid melting and solidification rates of the DMLS fabrication and the strict thermomechanical process of fabrication of the CNC blocks.

The microstructure of Co-Cr alloy is strongly associated with the mechanical properties and the chemical composition of the alloy (Koutsoukis et al., 2015; Sakaguchi & Powers, 2012). The different mechanical behaviour of the tested alloys previously reported in this paper is justified by their microstructure; hence the importance of further evaluating the element composition and phases of each tested alloy.

### 4.2.2 Energy dispersive x-ray analysis (EDX)

The element composition provided by each manufacture is shown in Table 1. The results of the Energy dispersive x-ray analysis (EDX) performed in this study (Table 3) are only slightly divergent of the composition provided by the manufacture which could be the result of different measuring methods. In addition, the chemical composition of the three tested groups is not the same because a single alloy for different fabrication methods is not commercially available. (Kim et al., 2016)

As seen in all tested groups, Co is the main constituent followed by Cr as the primary alloying element. As pointed out by Al Jabbari (2014), the first element mentioned should be the most predominant. The alloy should therefore be referred to as Co-Cr instead of Cr-Co, although it is not uncommon for authors to name it as Cr-Co.

Cobalt (Co) is believed to play an important role in the mechanical properties of the Co-Cr alloy as it introduces an unstable face-centered cubic crystal (fcc) structure that is retained at room temperature. In addition, when stresses are generated (e.g., rise in temperature) the fcc structure tends to transform to hexagonal close-packed (hcp) crystal structure giving the alloy the ability to absorb stresses and avoid damage.

As the main alloying element, Cr enhances resistance to corrosion and oxidation through carbide formation. On the other hand, addition of Cr should be done with caution as it may lead to the formation of a hard and brittle phase that decreases corrosion resistance. As seen in table 3, the three tested alloys have adequate Co and Cr composition.

Molybdenum (Mo) in a Co-Cr alloy is responsible for providing additional strength, increased corrosion resistance, and participates in the formation of carbides. Historically less commonly used in the dental industry, Tungsten (W) provides the same effect and can be used as a replacement of Mo (Al Jabbari, 2014). As shown in table 3, CNC has little to no traces of Mo, but in contrast it is the only alloy that contains W. The CNC alloy displayed the lowest values for strength and hardness, suggesting that Mo might be a better element to add strength to Co-Cr alloys than W possibly because of the precipitation of carbides known to increase strength and hardness. Another possible explanation has been suggested by Kim and coworkers (2016) who justified the decrease in mechanical properties by W or Mo segregation in the intermetallic compounds rather than being dispersed within the matrix.(Kim et al., 2016)

Even though carbide formation provides the primary strengthening mechanism for Co-Cr alloys (Herö et al., 1984), the ISO specification does not mandate the exact composition of trace of Carbon (C). This explains the reason why table 1 does not contain C traces information as well as the fact that C was not included in the present study evaluation. Further analysis of carbide formation is recommended for better evaluation of mechanical behaviors and alloy microstructure.

### 4.2.2X-ray diffraction analysis (XRD)

The XRD diagrams obtained for each group is shown in Figure 5. Figure 6 illustrated the XRD results for a CAST sample in 0 and 90 degrees for better visualization of the phases.

Pure cobalt (Co) when cooled extremely slowly transforms from a face-centered cubic (fcc) phase to a hexagonal close-packed (hcp) phase. The temperature needed for phase transformation for a Co alloy is higher than for pure Co which allows for the unstable fcc phase to be maintained at room temperature in a Co alloy. The fcc phase is believed to contribute to mechanical properties of the alloy such as high yield strength, high plasticity, higher fatigue resistance, and stress absorption propertied (through transformation of fcc to hcp structure).(Al Jabbari, 2014)

Chromium (Cr) as an alloying element increases strength due to carbide formation (any metal plus carbon - $C_3$ and $C_6$). Despite its beneficial increase in strength, Cr addition to the Co alloy should be made cautiously as it also leads to the formation of a harmful sigma (σ) phase which decreases corrosion resistance.

In addition to the dominant face-centered cubic (fcc) phase, a small amount hexagonal close-packed (hcp) phase was also identified in all groups. As none of the tested groups passed through a heat treatment, the presence of a dominant fcc phase is evident as hcp transformation does not often happen during normal cooling (absence of heat treatment). (Lee et al., 2022) More fcc peaks were found on the DLMS and CNC group which explains the increased plasticity of the samples as seen in the elongation test.

A peak of σ phase (intermetallic compound) was identified exclusively in the CAST group. The σ phase is a consequence of the heat process of the casting technique. Although able to increase the hardness of the alloy, the σ phase is considered harmful as it deteriorates the corrosion resistance properties of the alloy by promoting accumulation of Mo (or W) and Cr in the σ phase. Thus, the σ phase is not desirable as it increased wear and corrosion. (Qi et al., 2023)

No carbide phases were identified, possibly because of its small intensity, but further metallurgical analysis may be beneficial to explore the carbide phases present on each alloy as carbides are known to change the mechanical behavior and microstructure of Co-Cr alloys.

The higher amount of fcc phase and the absence of a σ phase, identified through XRD in the DLMS group, the small grain size and homogeneous surface seen in the SEM analyses and the presence of Mo found through EDX in the alloy justify the remarkable increase in mechanical properties of the DLMS group seen in this study.

## Limitations:

The limitations of the present study include:

- Co-Cr alloys tested did not have identical chemical composition which makes direct comparison hard.
- Different process parameters such as build direction, metal particle size, and laser melting rate were not taken into consideration.

## Future recommendations

- Carbon identification to evaluate carbide influence on mechanical properties and microstructure.
- Evaluation of heat treatment on microstructure and mechanical behavior of Co-Cr alloys fabricated by CAST, CNC and DMLS.

# CHAPTER 5

## Conclusion

Based on the findings of the present in vitro study, the following conclusions can be drawn:

1- The mechanical properties of the tested Co-Cr alloys used in dentistry were dependent of the fabrication method.

2- Overall, DMLS presented the best mechanical properties as it displayed higher elastic limit, strength, and hardness when compared to CAST and CNC. CNC presented the lowest values for elastic limit, strength, and hardness, and the highest ductility.

3- The microstructure of the tested Co-Cr alloys used in dentistry were dependent of the fabrication method.

# REFERENCES

Aboulkhair, N. T., Simonelli, M., Parry, L., Ashcroft, I., Tuck, C., & Hague, R. (2019). 3D printing of Aluminium alloys: Additive Manufacturing of Aluminium alloys using selective laser melting. *Progress in Materials Science*, *106*, 100578. https://doi.org/https://doi.org/10.1016/j.pmatsci.2019.100578

Ahn, D.-G. (2016). Direct metal additive manufacturing processes and their sustainable applications for green technology: A review. *International Journal of Precision Engineering and Manufacturing-Green Technology*, *3*, 381–395. https://doi.org/10.1007/s40684-016-0048-9

Al Jabbari, Y. (2014). Physico-mechanical properties and prosthodontic applications of Co-Cr dental alloys: A review of the literature. *The Journal of Advanced Prosthodontics*, *6*, 138–145. https://doi.org/10.4047/jap.2014.6.2.138

Al Jabbari, Y. S., Koutsoukis, T., Barmpagadaki, X., & Zinelis, S. (2014). Metallurgical and interfacial characterization of PFM Co–Cr dental alloys fabricated via casting, milling or selective laser melting. *Dental Materials*, *30*(4), e79–e88. https://doi.org/https://doi.org/10.1016/j.dental.2014.01.008

Alageel, O., Abdallah, M.-N., Alsheghri, A., Song, J., Caron, E., & Tamimi, F. (2018). Removable partial denture alloys processed by laser-sintering technique. *Journal of Biomedical Materials Research Part B: Applied Biomaterials*, *106*(3), 1174–1185. https://doi.org/https://doi.org/10.1002/jbm.b.33929

Alhallak, K., & Nankali, A. (2021). 3D Printing Technologies for Removable Dentures Manufacturing: A Review of Potentials and Challenges. *The European Journal of Prosthodontics and Restorative Dentistry*, *30*. https://doi.org/10.1922/EJPRD_2208Alhallak06

Almufleh, B., Emami, E., Alageel, O., de Melo, F., Seng, F., Caron, E., Nader, S. A., Al-Hashedi, A., Albuquerque, R., Feine, J., & Tamimi, F. (2018). Patient satisfaction with laser-sintered removable partial dentures: A crossover pilot clinical trial. *The Journal of Prosthetic Dentistry*, *119*(4), 560-567.e1. https://doi.org/https://doi.org/10.1016/j.prosdent.2017.04.021

Bae, S.-Y., Park, J.-Y., Kim, J.-H., Kim, H.-Y., Kim, M.-B., & Kim, W.-C. (2015). The comparison of accuracy on three-unit fixed dental prosthesis made with CAD/CAM milling machines. *Journal of Korean Acedemy of Dental Technology*, *37*, 9–15. https://doi.org/10.14347/kadt.2015.37.1.9

Craig, R. G., & Hanks, C. T. (1988). Reaction of fibroblasts to various dental casting alloys. *Journal of Oral Pathology & Medicine*, *17*(7), 341–347. https://doi.org/https://doi.org/10.1111/j.1600-0714.1988.tb01547.x

Dolgov, N., Dikova, T., Dzhendov, D., Pavlova, D., & Simov, M. (2016). Mechanical Properties of Dental Co-Cr Alloys Fabricated via Casting and Selective Laser Melting. *International Journal "Materials Science. Non-Equilibrium Phase Transformations,"* 3–7.

Evans, E. J., & Thomas, I. T. (1986). The in vitro toxicity of cobalt-chrome-molybdenum alloy and its constituent metals. *Biomaterials*, *7*(1), 25–29. https://doi.org/https://doi.org/10.1016/0142-9612(86)90084-0

Han, X., Sawada, T., Schille, C., Schweizer, E., Scheideler, L., Geis-Gerstorfer, J., Rupp, F., & Spintzyk, S. (2018). Comparative Analysis of Mechanical Properties and Metal-Ceramic Bond Strength of Co-Cr Dental Alloy Fabricated by Different Manufacturing Processes. *Materials*, *11*, 1801. https://doi.org/10.3390/ma11101801

Herö, H., Syverud, M., Gjönnes, J., & Horst, J. A. (1984). Ductility and structure of some cobalt-base dental casting alloys. *Biomaterials*, *5*(4), 201–208. https://doi.org/https://doi.org/10.1016/0142-9612(84)90016-4

Hong, J.-K., Kim, S.-K., Heo, S.-J., & Koak, J.-Y. (2020). Mechanical Properties and Metal-Ceramic Bond Strength of Co-Cr Alloy Manufactured by Selective Laser Melting. *Materials*, *13*, 5745. https://doi.org/10.3390/ma13245745

Hong, M.-H., Lee, D.-H., Hanawa, T., & Kwon, T.-Y. (2022). Comparison of microstructures and mechanical properties of 3 cobalt-chromium alloys fabricated with soft metal milling technology. *The Journal of Prosthetic Dentistry*, *127*(3), 489–496. https://doi.org/https://doi.org/10.1016/j.prosdent.2020.07.037

Kim, H., Jang, S.-H., Kim, Y., Son, J., Min, B.-K., Kim, K.-H., & Kwon, T.-Y. (2016). Microstructures and Mechanical Properties of Co-Cr Dental Alloys Fabricated by Three CAD/CAM-Based Processing Techniques. *Materials*, *9*, 596. https://doi.org/10.3390/ma9070596

Kim, K.-B., Kim, J.-H., Kim, W.-C., & Kim, J.-H. (2014). Three-dimensional evaluation of gaps associated with fixed dental prostheses fabricated with new technologies. *The Journal of*

*Prosthetic Dentistry*, *112*(6), 1432–1436. https://doi.org/https://doi.org/10.1016/j.prosdent.2014.07.002

Konieczny, B., Szczesio-Włodarczyk, A., Sokołowski, J., & Bociong, K. (2020). Challenges of Co–Cr Alloy Additive Manufacturing Methods in Dentistry—The Current State of Knowledge (Systematic Review). *Materials*, *13*, 3524. https://doi.org/10.3390/ma13163524

Koutsoukis, T., Zinelis, S., Eliades, G., Al-Wazzan, K., Rifaiy, M. Al, & Al Jabbari, Y. S. (2015). Selective Laser Melting Technique of Co-Cr Dental Alloys: A Review of Structure and Properties and Comparative Analysis with Other Available Techniques. *Journal of Prosthodontics*, *24*(4), 303–312. https://doi.org/https://doi.org/10.1111/jopr.12268

Krug, K.-P., Knauber, A., & Nothdurft, F. (2014). Fracture behavior of metal-ceramic fixed dental prostheses with frameworks from cast or a newly developed sintered cobalt-chromium alloy. *Clinical Oral Investigations*, *19*. https://doi.org/10.1007/s00784-014-1233-2

Kruth, J.-P., Mercelis, P., Vaerenbergh, J., Froyen, L., & Rombouts, M. (2005). Binding Mechanisms in Selective Laser Sintering and Selective Laser Melting. *Rapid Prototyping Journal*, *11*, 26–36. https://doi.org/10.1108/13552540510573365

Lebon, N., Tapie, L., Duret, F., & Attal, J.-P. (2016). Understanding dental CAD/CAM for restorations - Dental milling machines from a mechanical engineering viewpoint. Part B: Labside milling machines. *International Journal of Computerized Dentistry*, *19*, 115–134.

Lee, W.-F., Wang, J.-C., Hsu, C.-Y., & Peng, P.-W. (2022). Microstructure, mechanical properties, and retentive forces of cobalt-chromium removable partial denture frameworks fabricated by selective laser melting followed by heat treatment. *The Journal of Prosthetic Dentistry*, *127*(1), 115–121. https://doi.org/https://doi.org/10.1016/j.prosdent.2020.06.038

Myszka, D., & Skrodzki, M. (2016). Comparison of Dental Prostheses Cast and Sintered by SLM from Co-Cr-Mo-W Alloy. *Archives of Foundry Engineering*, *16*, 201–207. https://doi.org/10.1515/afe-2016-0110

Øilo, M., Nesse, H., Lundberg, O. J., & Gjerdet, N. R. (2018). Mechanical properties of cobalt-chromium 3-unit fixed dental prostheses fabricated by casting, milling, and additive manufacturing. *The Journal of Prosthetic Dentistry*, *120*(1), 156.e1-156.e7. https://doi.org/https://doi.org/10.1016/j.prosdent.2017.12.007

Okazaki, Ishino, & Higuchi. (2019). Chemical, Physical, and Mechanical Properties and Microstructures of Laser-Sintered Co–25Cr–5Mo–5W (SP2) and W–Free Co–28Cr–6Mo Alloys for Dental Applications. *Materials*, *12*, 4039. https://doi.org/10.3390/ma12244039

Oliveira, T., & Reis, A. (2019). Fabrication of dental implants by the additive manufacturing method: A systematic review. *The Journal of Prosthetic Dentistry*, *122*. https://doi.org/10.1016/j.prosdent.2019.01.018

Qi, J., Ma, L., Gong, P., & Rainforth, W. M. (2023). Investigation of the wear transition in CoCrMo alloys after heat treatment to produce an HCP structure. *Wear*, *518–519*, 204649. https://doi.org/https://doi.org/10.1016/j.wear.2023.204649

Revilla-León, M., Al-Haj Husain, N., Methani, M. M., & Özcan, M. (2021). Chemical composition, surface roughness, and ceramic bond strength of additively manufactured cobalt-chromium dental alloys. *The Journal of Prosthetic Dentistry*, *125*(5), 825–831. https://doi.org/https://doi.org/10.1016/j.prosdent.2020.03.012

Revilla-León, M., & Özcan, M. (2017). Additive Manufacturing Technologies Used for 3D Metal Printing in Dentistry. *Current Oral Health Reports*, *4*, 1–8. https://doi.org/10.1007/s40496-017-0152-0

Revilla-León, M., Sadeghpour, M., & Özcan, M. (2020). A Review of the Applications of Additive Manufacturing Technologies Used to Fabricate Metals in Implant Dentistry. *Journal of Prosthodontics*, *29*. https://doi.org/10.1111/jopr.13212

Sakaguchi, R. L., & Powers, J. M. (2012). *Craig's Restorative Dental Materials*. Elsevier. https://books.google.ca/books?id=P1wTdCEHo5EC

Strub, J. R., Rekow, E. D., & Witkowski, S. (2006). Computer-aided design and fabrication of dental restorations: Current systems and future possibilities. *The Journal of the American Dental Association*, *137*(9), 1289–1296. https://doi.org/https://doi.org/10.14219/jada.archive.2006.0389

Sulaiman, T. (2020). Materials in digital dentistry—A review. *Journal of Esthetic and Restorative Dentistry*, *32*. https://doi.org/10.1111/jerd.12566

Takaichi, A., Suyalatu, Nakamoto, T., Joko, N., Nomura, N., Tsutsumi, Y., Migita, S., Doi, H., Kurosu, S., Chiba, A., Wakabayashi, N., Igarashi, Y., & Hanawa, T. (2013). Microstructures and mechanical properties of Co–29Cr–6Mo alloy fabricated by selective laser melting process for dental applications. *Journal of the Mechanical Behavior of Biomedical Materials*, *21*, 67–76. https://doi.org/https://doi.org/10.1016/j.jmbbm.2013.01.021

Viennot, S., Dalard, F., Lissac, M., & Grosgogeat, B. (2005). Corrosion resistance of cobalt-chromium and palladium-silver alloys used in fixed prosthetic restorations. *European Journal of Oral Sciences*, *113*, 90–95. https://doi.org/10.1111/j.1600-0722.2005.00190.x

Wang, H., Feng, Q., Li, N., & Xu, S. (2016). Evaluation of metal-ceramic bond characteristics of three dental Co-Cr alloys prepared with different fabrication techniques. *The Journal of Prosthetic Dentistry*, *116*. https://doi.org/10.1016/j.prosdent.2016.06.002

Wataha, J. C., & Messer, R. L. (2004). Casting alloys. *Dental Clinics of North America*, *48*(2), 499–512. https://doi.org/https://doi.org/10.1016/j.cden.2003.12.010

Wu, L., Zhu, H., Gai, X., & Wang, Y. (2014). Evaluation of the mechanical properties and porcelain bond strength of cobalt-chromium dental alloy fabricated by selective laser melting. *The Journal of Prosthetic Dentistry*, *111*(1), 51–55. https://doi.org/https://doi.org/10.1016/j.prosdent.2013.09.011

Wu, M., Dong, X., Qu, Y., Yan, J., & Li, N. (2022). Analysis of microstructure and fatigue of cast versus selective laser-melted dental Co-Cr alloy. *The Journal of Prosthetic Dentistry*, *128*(2), 218.e1-218.e7. https://doi.org/https://doi.org/10.1016/j.prosdent.2022.05.011

Xing, X., Hu, Q., Liu, Y., Wang, Y., & Cheng, H. (2022). Comparative analysis of the surface properties and corrosion resistance of Co-Cr dental alloys fabricated by different methods.

*The Journal of Prosthetic Dentistry*, *127*(3), 497.e1-497.e11. https://doi.org/https://doi.org/10.1016/j.prosdent.2021.11.019

Yu, J.-M., Kang, S.-Y., Lee, J.-S., Jeong, H.-S., & Lee, S.-Y. (2021). Mechanical Properties of Dental Alloys According to Manufacturing Process. *Materials*, *14*, 3367. https://doi.org/10.3390/ma14123367

Zhou, Y., Li, N., Yan, J., & Zeng, Q. (2018). Comparative analysis of the microstructures and mechanical properties of Co-Cr dental alloys fabricated by different methods. *The Journal of Prosthetic Dentistry*, *120*(4), 617–623. https://doi.org/https://doi.org/10.1016/j.prosdent.2017.11.015

## *Appendix 1. Journal Article Manuscript for Journal of Prosthetic Dentistry*

# Assessment of mechanical properties and microstructure of Co-Cr dental alloys manufactured by casting, milling, and 3D printing

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## ACKNOWLEDGMENTS

The authors thank Cross-town Dental Laboratory and 3DRPD for their contribution with the casted and printed specimens, the Industrial Technology Centre for their collaboration with the mechanical tests, and Dr Charlene Solomon for her assistance with preparing this manuscript.

## ABSTRACT

### Statement of problem

Mechanical properties and microstructure of Co-Cr alloys must be considered when choosing the best alloy for each clinical situation. More information is needed on the digital manufacturing methods for metals in dentistry such as computer numerical control, and direct laser metal sintering.

### Purpose

The aim of this study is to investigate the effect of the three different Co-Cr manufacturing processes on the mechanical properties and microstructure of Co-Cr dental alloys.

### Materials and methods

Dumbbell-shaped specimens (n=6) were fabricated with CAST, CNC, and DMLS techniques. Tensile test, 3-point-bending test, and microhardness were performed. Microstructure was evaluated through scanning electron microscopy, energy dispersive X-ray analysis, and X-ray diffraction analysis. ANOVA test followed by post hoc Tukey tests was done for statistical analysis.

### Results

DMLS showed the highest values for 0.2% yield strength (908.0±13.1MPa), tensile strength (1123.7±6.5MPa), flexural strength (2273.0±43.2MPa), and microhardness (438.2±44.9HV) followed by CAST and CNC. No statistical differences found for elongation between CNC and DMLS, or DMLS and CAST ($P>.05$). No statistical differences found for elastic modulus among

all groups (P>.05). EDX reveled a slightly different chemical composition among the groups. XRD showed face-centered cubic as the dominant phase and a small amount of hexagonal close-packed in all groups. A peak of σ phase was identified in the CAST group.

## Conclusions

The mechanical properties and microstructures of Co-Cr dental alloys is dependent on the fabrication method.

## Clinical implications

The improved mechanical and microstructure characteristics of Co-Cr alloy manufactured through DMLS may suggest better clinical outcomes.

## INTRODUCTION:

Cobalt-Chromium (Co-Cr) alloys are one of the most used metal alloys used in prosthetic dentistry(1,2) from removable prosthesis framework to fixed metal-ceramic restoration. Co-Cr alloys are a relatively inexpensive replacement for noble alloys (2,3) and the most common alternative for use in individuals with nickel allergy.(2,4) Known for their high strength,(5) high modulus of elasticity,(5) and favorable corrosion and tarnish resistance,(6,7) Co-Cr alloys are favorable to wear resistance, longevity, and highly biocompatible.(8)

The lost wax casting (LWC) technique has been in use since 1907 and is still a common fabrication method in the dental industry.(1,9) This method is, however, progressively losing its popularity due to being time consuming, technique sensitive,(10) and hard to manipulate in the dental laboratory due to the high melting temperature of Co-Cr alloys.(11) This conventional fabrication method has unavoidable distortion of the wax pattern and inherent structural defects caused by the melting and cooling characteristics of the alloy.(11)

Computer-aided design and computer-aided manufacturing (CAD-CAM) was introduced to the dental field in the early 1980s and has been shown to reduce flaws of the conventional fabrication method.(12,13) This technology comprises two main categories: subtractive manufacturing process (SM), and additive manufacturing (AM).

The SM is a computer numerical control (CNC) milling process that grinds a block into the desired shape improving the precision of the framework (14) while reducing the manufacturing time. One of the major advantages of SM is the substantial reduction of porosity (4) of the final object as the metal disk is manufactured under high industrial standards.(15) However, this process leads to a high waste of tools and materials (16) and presents a limitation in manufacturing complex objects due to the limited movement of their axis.(17,18)

The AM technology allows complex 3D object to be fabricated in a short period of time(3) with little or no porosity, (4,19) no residual stress due to the heat treatment applied,(20,21) high dimensional accuracy, (19,22) and considerably less material waste then the SM process.(17) It has also been reported to provide higher patient satisfaction for the fabrication of partial frameworks when compared to conventional methods.(23) Powder bed fusion (PBF) is the most commonly employed AM technology for metal processing in dentistry; (9,22,24,25) it can be subdivided into three main methods: selective laser sintering (SLS), selective laser melting (SLM), and electron beam melting (EBM). SLS uses laser energy to heat and fuse the metal powder into a thin solid layer (20-100 μm) (26) without fully melting the metal powder,(20) while SLM and EBM fully melt the metal powder.(1,2,9) The main difference between SLM and EBM is the energy source (laser or electron bean).(2) Direct Metal Laser Sintering (DMLS) is also a variation of PBF and that uses a mixture of metal powders with high and low melting temperatures.(22) During the processing procedure the metal powder with low melting temperature fully melts while the high melting temperature powder only melts partially.(27,28) The major disadvantage of AM technology is the high manufacturing cost which restricts this method to few specific CAD/CAM centers in the dental industry.(29)

Different authors reported that different manufacturing methods result in metal alloys with different microstructures (1,2,4,30–32) and mechanical properties.(16,19,31–37) However, the available data on the microstructure and mechanical properties of Cobalt-Chromium alloy fabricated by SM and AM technologies used in dentistry is still limited.(3,25,26) With their increased use in the dental industry, it is crucial to have more understanding and information on the digital manufacturing processes. Thus, the aim of this paper is to investigate the effect of the three different Co-Cr manufacturing processes on the mechanical properties and microstructure of the alloys. The null hypothesis is that there is no significant difference in the mechanical properties and microstructures resulting from different manufacturing processes.

## MATERIALS AND METHODS:

Three commercially available Co-Cr alloys were tested. Composition and manufacturer information are listed on Table 1. Dumbbell-shaped specimens (n=6) were designed according to ISO 22674 (Figure 1) using a proprietary AutoCAD software. The design was converted into a standard tessellation language (.stl) format and used for the fabrication of the specimens according to each manufacturer's instruction.

The CAST group specimens were fabricated by the lost-wax technique from a printed castable wax pattern. The .stl file was used to fabricate a wax pattern with the same exact dimensions as the other groups. Printed wax patterns were fabricated on an SLA printer (Form 3, Formlabs, Somerville, MA, USA) with a castable wax (Castable wax V1, Formlabs, Somerville, MA, USA), and invested (Wirovest, Bego, Quebec, QC, Canada) and casted using a Co-Cr ingot (Table 1) on a high-frequency centrifugal casting machine (Fornax T, Bego, Quebec, QC, Canada).

For the CNC group, specimens were milled using prefabricated Co-Cr alloy blank (Table 1) on a 5-axis milling machine (Roders RXD5, Roders TEC, Germany). In the DMLS group, specimens were fabricated by transferring the .stl file to a high-performance 3D printer (ProX DMP 200 Dental, 3D Systems, Rock Hill, SC, USA) according to the settings recommended by the manufacturer and specimens were fabricated using cobalt-chromium alloy powder (Table 1).

Tensile test (n=6) was carried out at room temperature for the measurement of 0.2% yield strength, tensile strength, elongation, and elastic modulus with a crosshead speed of 1.5mm/min using a Universal Testing Machine (UTM) (Landmark Servo-hydraulic Universal Test Machine Model 370.10, MTS Systems Corporation, Eden Prairie, MN, USA) with an attached extensometer (Miniature Axial Extensometers Model 3442MTS, Epsilon, Jackson, WY, USA). The gauge length of each specimen was accurately measured with a digital caliper (CD-6 ASX, Mitutoyo, Aurora, IL, USA) within the gauge length interval to 0.01mm. For the measurement of flexural strength, the UTM was used to perform a 3-point-bend test (n=6) at a crosshead speed of 1.5mm/min until failure.

For the microhardness test (n=6), the samples were mounted in phenolic resin (EasyFast, Struers Inc., Paris, France), ground with wet silicon carbide abrasive paper up to 2000 grit (LECO 8”, LECO, St. Joseph, MO, USA) and polished with 9µm, 6µm, and 3µm polycrystalline diamond suspension (MetaDi, Buehler, Lake Bluff, IL, USA). Microhardness was measured at 5 different spots on each specimen using a Vickers Hardness Tester (Micromet 5114, Buehler, Lake Bluff, IL, USA) with a load of 500gf and a dwell time of 20 seconds.

Following the microhardness test, specimens were etched for 30 seconds with hydrochloric acid/hydrogen peroxide (80:20 v/v) at room temperature.(4) Microstructure was analyzed (n=2) by scanning electron microscopy (SEM) (FEI Nova NanoSEM 450, FEI, Hillsboro, OR, USA) under an accelerating voltage of 20kV and spot analysis was performed with energy dispersive X-ray analysis (EDX) in three different spots per specimen to determine the element composition of each tested specimen.

Phase identification was performed (n=2) with an x-ray diffractometer (XRD) (Simens/Bruker

D5000, Bruker, Aubrey, Texas, USA) equipped with a sealed X-ray tube. Samples were pre-scanned from 15-40° 2θ. Data was collected in two sample positions (0 and 90 degrees) with an accelerating voltage of 40kV, a beam current of 35mA, 2θ scan range between 35-100 degrees, and in step-scan mode using 0.02-degree step and 2 s dwell time.

Statistical differences for the tensile test, 3-point-bending, and hardness were evaluated by one-way ANOVA followed by post hoc Tukey tests to determine the interaction among the groups. (Origin(Pro) 2023, OriginLab Corporation, MA, USA) Data was expressed as mean ±SEM. A *p* value of less than 0.05 was considered significant.

## RESULTS

Mechanical properties and microstructure of three commonly used techniques of manufacturing Cobalt-Chromium alloy in dentistry were analyzed.

Through the tensile test, 0.2% yield strength, tensile strength, elongation, and elastic modulus were calculated for each group. As seen in Table 2, 0.2% yield strength and tensile strength were higher for the DMLS group (908.0±13.1 MPa and 1123.7±6.5 MPa) than those of CNC (413.0±10.0 MPa and 533.1±17.4 MPa) and CAST (462.1±8.0 MPa and 632.6±23.7 MPa). Statistically significant differences were found between the groups tested ($p < 0.05$). Elongation values were statistically different for the CNC (15.3±3.9 %) and CAST (2.3±0.2 %) with no statistical difference between DMLS (10.1±0.6 %) and the other two groups. No statistically significant differences were found between the groups in the overall average value for elastic modulus ($p > 0.05$). 3-point bend test revealed the highest flexural strength for the DMLS group (2273.0±43.2 MPa), followed by CAST (1351.2±35.7 MPa) and CNC (1155.6±41.7 MPa). Statistically significant differences were found between the groups tested ($p < 0.05$).

The microhardness result values were highest for the DMLS (438.2±44.9 HV) group followed by CAST (400.0±33.3 HV) and lowest for CNC (295.0±22.1 HV) as seen in Table 2. Statistically significant differences were found between the tested groups ($p < 0.05$).

The representative SEM images of CAST, CNC, and DMLS are shown in Figure 2 with three different magnifications (x1000, x2000, x5000).

Table 3 illustrates the results of quantitative elemental spot analysis with EDX performed in 3 different spots on the same specimen. The greatest number of element types were found in the CNC group where tungsten (W) was found on an average of 7.0 wt% while no W was detected on CAST and DMLS. In addition, CNC presented the least percentage of Mo and Cr, CAST contained the highest percentage of Cr, and the greatest percentage of Co was found on the DMLS group. Co was the main element found in all teste alloys followed by Cr.

The X-ray diffraction analysis (XRD) spectra of the three tested groups is displayed in Figure 3. Face-centered cubic (fcc) and hexagonal close-packed (hcp) were the main alloy phases present in all three tested groups. The fcc phase was the dominant phase with a small amount of hcp. In addition, a peak of $\sigma$ phase (intermetallic compound) was identified exclusively in the CAST group.

## DISCUSSION

The present in vitro study investigated and compared the mechanical properties and microstructure of Co-Cr dental alloy fabricated by three different manufacturing methods (casting, additive, and subtractive manufacturing). In agreement with previous studies (31,32) the present findings showed that the mechanical properties and microstructures of the tested alloys were dependent on the manufacturing method, thus the null hypothesis was rejected.

The ISO 22674:2016 classifies metallic materials that are suitable for the fabrication of dental restorations and appliances and specifies their mechanical requirements. Table 4 shows that all alloys satisfy the mechanical properties specified by the ISO 22674. DMLS is classified as type 5 (0.2% yield strength: >500 MPa; elongation: >2%; elastic modulus: >150 GPa) while CNC and CAST are classified as type 4 (due to 0.2% yield strength: <500 but >360MPa).

Overall, Co-Cr dental alloy fabricated with DMLS presented statistically significant higher mechanical properties than CAST and CNC (table 2). All tested alloys have enough yield strength to withstand permanent deformation (more than 300 MPa), although the high 0.2% yield strength of the DMLS group would alloy for the design of a thinner cross-section without compromising rigidity (5) and a slower loosening of clasp retention due to insertion and removal of a RPD framework as plastic deformation requires a higher stress load when compared to the other tested groups. (31) High tensile strength as well as high flexural strength are desirable properties as higher forces are needed to lead to fracture. DLMS presented significantly higher tensile and flexural forces when compared to CNC and CAST. In accordance with the results of this study and previous literature, (1) higher strength values for AM alloys have been attributed to the differences in chemical composition and processing parameters.

CNC had the highest elongation values although not statistically different than DMLS. This behaviour can be explained by the presence of a higher amount of face-centered cubic (fcc) phase of the DLMS and CNC groups when compared to the CAST group. The present results suggest that all tested alloys provide adequate ductility with CNC and DMLS offering statistically similar workability, while CAST has a slightly more brittle behavior. All tested methods of fabrication generated similar elastic modulus showing that no benefits of one over another was reported for this mechanical property.

DMLS displayed the highest values for hardness offering the best resistance to permanent distortion and scratching. The high hardness values of DLMS can be attributed to the sintering process which has been previously reported to reduce porosity (19,30) and provide a more refined grain structure (1) due to the residual stresses generated.  In contrast, CNC presented almost half of DMLS hardness which could be explained by the chemical composition (presence of W instead of Mo) of the alloys.

Previous literature has shown that, in comparison to CNC and CAST samples, AM samples present a finer grain structure. (1,32) The more homogeneous surface, as seen in Figure 2, as well as the improved grain refinement of AM samples explain the enhancement in ductility and toughness, which is the main reason for improved mechanical performance of DMLS samples. The mechanical results of the present study are in accordance with other in vitro studies (1,31) that also reported overall higher mechanical properties for the AM group.

Figure 2 shows a representation of SEM images of the Co-Cr specimens. Even though the etching protocol used for this test did not allow for the clear identification of the grain boundaries, the images obtained reveled a different microstructure pattern between the groups indicating that the three tested manufacturing methods affected the specimen’s microstructures. The CAST specimens showed a typical dendritic structure (Figure 4 A – red arrow) characteristic of the slow cooling and solidification rates. The DMLS and CNC revealed a more homogeneous surface which is explained by the rapid melting and solidification rates of the DMLS fabrication and the strict thermomechanical process of fabrication of the CNC blocks.

The element composition provided by each manufacture is shown in Table 1. The results of the Energy dispersive x-ray analysis (EDX) performed in this study (table 3) are only slightly divergent of the composition provided by the manufacture which could be the result of different measuring methods. In addition, the chemical composition of the three tested groups is not the same because a single alloy for different fabrication methods is not commercially available. (31)

Co is the main constituent of all tested groups followed by Cr as the primary alloying element. Co is believed to play an important role in the mechanical properties of the Co-Cr alloy as it introduces an unstable face-centered cubic crystal (fcc) structure that is retained in room temperature. In addition, when stresses are generated (e.g. rise in temperature) the fcc structure tends to transform to hexagonal close-packed (hcp) crystal structure giving the alloy the ability to absorb stresses and avoid damage. As the main alloying element, Cr enhances resistance to corrosion and oxidation through carbide formation. All tested alloys have adequate Co and Cr composition.

Molybdenum (Mo) in a Co-Cr alloy is responsible for providing additional strength, increased corrosion resistance, and participates in the formation of carbides. Historically less commonly used in the dental industry, Tungsten (W) provides the same effect and can be used as a replacement of Mo (5). CNC has little to no traces of Mo, but in contrast it is the only alloy that contains W. CNC displayed the lowest values for strength and hardness, suggesting that Mo might be a better element to add strength to Co-Cr alloys than W possibly because of the precipitation of carbides known to increase strength and hardness. Another possible explanation has been suggested by Kim et al who justified the decrease in mechanical properties by W or Mo segregation in the intermetallic compounds rather than being dispersed within the matrix.(31)

Even though carbide formation provides the primary strengthening mechanism for Co-Cr alloys, the ISO specification does not mandate the exact composition of trace of Carbon (C). This explains the fact that C was not included in the present study. Further analysis of carbide formation is recommended for better evaluation of mechanical behaviors and alloy microstructure.

The XRD diagrams obtained for each group is shown in Figure 3. In addition to the dominant face-centered cubic (fcc) phase, a small amount hexagonal close-packed (hcp) phase was identified in all groups. As none of the tested groups passed through a heat treatment, the presence of a dominant fcc phase is evident as hcp transformation does not often happen during normal cooling (absence of heat treatment). (21) More fcc peaks were found on the DLMS and CNC group which explains the increased plasticity of the samples as seen in the elongation test.

A peak of σ phase (intermetallic compound) was identified exclusively in the CAST group. The σ phase is a consequence of the heat process of the casting technique. Although able to increase the hardness of the alloy, the σ phase is considered harmful as it deteriorates the corrosion resistance properties of the alloy by promoting accumulation of Mo (or W) and Cr in the σ phase. Thus, the σ phase is not desirable as it increased wear and corrosion. (38) No carbide phases were identified, possibly because of its small intensity, but further metallurgical analysis may be beneficial to explore the carbide phases present on each alloy as carbides are known to change the mechanical behavior and microstructure of Co-Cr alloys.

The higher amount of fcc phase and the absence of a σ phase, identified through XRD in the DLMS group, the small grain size and homogeneous surface seen in the SEM analyses and the presence of Mo found through EDX in the alloy justify the remarkable increase in mechanical properties of the DLMS group seen in this study. Despite the promising mechanical properties of the DMLS, it has been suggested that mechanical properties and microstructure can be affected by other factors such as building direction, metal particle size, and melting speed of the laser (39) and therefore results should be interpreted with caution. Other important factors such as resistance to corrosion and tarnish, metal-ceramic bonding, biocompatibility, and fit must also be further investigated so the newer technologies can safely, and predictability replace the traditional casting technique.

## CONCLUSION

Based on the findings of the present in vitro study, the following conclusions can be drawn:

1- The mechanical properties of the tested Co-Cr alloys used in dentistry were dependent of the fabrication method.

2- Overall, DMLS presented the best mechanical properties as it displayed higher elastic limit, strength, and hardness when compared to CAST and CNC. CNC presented the lowest values for elastic limit, strength, and hardness, and the highest ductility.

3- The microstructure of the tested Co-Cr alloys used in dentistry were dependent of the fabrication method.

## REFERENCES

1. Wu M, Dong X, Qu Y, Yan J, Li N. Analysis of microstructure and fatigue of cast versus selective laser-melted dental Co-Cr alloy. J Prosthet Dent. 2022;128(2):218.e1-218.e7. doi:10.1016/j.prosdent.2022.05.011

2. Revilla-León M, Al-Haj Husain N, Methani MM, Özcan M. Chemical composition, surface roughness, and ceramic bond strength of additively manufactured cobalt-chromium dental alloys. *J Prosthet Dent*. 2021;125(5):825-831. doi:10.1016/j.prosdent.2020.03.012

3. Sulaiman TA. Materials in digital dentistry-A review. *J Esthet Restor Dent*. 2020;32(2):171-181. doi:10.1111/jerd.12566

4. Xing X, Hu Q, Liu Y, Wang Y, Cheng H. Comparative analysis of the surface properties and corrosion resistance of Co-Cr dental alloys fabricated by different methods. *J Prosthet Dent*. 2022;127(3):497.e1-497.e11. doi:10.1016/j.prosdent.2021.11.019

5. Al Jabbari YS. Physico-mechanical properties and prosthodontic applications of Co-Cr dental alloys: a review of the literature. *J Adv Prosthodont*. 2014;6(2):138-145. doi:10.4047/jap.2014.6.2.138

6. Viennot S, Dalard F, Lissac M, Grosgogeat B. Corrosion resistance of cobalt-chromium and palladium-silver alloys used in fixed prosthetic restorations. *Eur J Oral Sci*. 2005;113(1):90-95. doi:10.1111/j.1600-0722.2005.00190.x

7. Uriciuc WA, Boșca AB, Băbțan AM, et al. Study on the Surface of Cobalt-Chromium Dental Alloys and Their Behavior in Oral Cavity as Cast Materials. *Materials (Basel)*. 2022;15(9):3052. doi:10.3390/ma15093052

8. Evans EJ, Thomas IT. The in vitro toxicity of cobalt-chrome-molybdenum alloy and its constituent metals. *Biomaterials*. 1986;7(1):25-29. doi:10.1016/0142-9612(86)90084-0

9. Myszka D, Skrodzki M. Comparison of Dental Prostheses Cast and Sintered by SLM from Co-Cr-Mo-W Alloy. *Archives of Foundry Engineering*. 2016;16:201–7. doi: 10.1515/afe-2016-0110

10. Kim KB, Kim JH, Kim WC, Kim JH. Three-dimensional evaluation of gaps associated with fixed dental prostheses fabricated with new technologies. *J Prosthet Dent*. 2014;112(6):1432-1436. doi:10.1016/j.prosdent.2014.07.002

11. Wataha JC, Messer RL. Casting alloys. *Dent Clin North Am*. 2004;48(2):vii-512. doi:10.1016/j.cden.2003.12.010

12. Han X, Sawada T, Schille C, et al. Comparative Analysis of Mechanical Properties and Metal-Ceramic Bond Strength of Co-Cr Dental Alloy Fabricated by Different Manufacturing Processes. *Materials (Basel)*. 2018;11(10):1801. doi:10.3390/ma11101801

13. Alhallak KR, Nankali A. 3D Printing Technologies for Removable Dentures Manufacturing: A Review of Potentials and Challenges. *Eur J Prosthodont Restor Dent*. 2022;30(1):14-19. doi:10.1922/EJPRD_2208Alhallak06

14. Bae SY, Park JY, Kim JH, Kim HY, Kim MB, Kim WC. The comparison of accuracy on three-unit fixed dental prosthesis made with CAD/CAM milling machines. *Journal of Korean Acedemy of Dental Technology*. 2015; 37:9–15. doi: 10.14347/kadt.2015.37.1.9

15. Koutsoukis T, Zinelis S, Eliades G, Al-Wazzan K, Rifaiy MA, Al Jabbari YS. Selective Laser Melting Technique of Co-Cr Dental Alloys: A Review of Structure and Properties and Comparative Analysis with Other Available Techniques. *J Prosthodont*. 2015;24(4):303-312. doi:10.1111/jopr.12268

16. Yu JM, Kang SY, Lee JS, Jeong HS, Lee SY. Mechanical Properties of Dental Alloys According to Manufacturing Process. *Materials (Basel)*. 2021;14(12):3367. doi:10.3390/ma14123367

17. Strub JR, Rekow ED, Witkowski S. Computer-aided design and fabrication of dental restorations: current systems and future possibilities. *J Am Dent Assoc*. 2006;137(9):1289-1296. doi:10.14219/jada.archive.2006.0389

18. Lebon N, Tapie L, Duret F, Attal JP. Understanding dental CAD/CAM for restorations--dental milling machines from a mechanical engineering viewpoint. Part B: labside milling machines. *Int J Comput Dent*. 2016;19(2):115-134.

19. Wu L, Zhu H, Gai X, Wang Y. Evaluation of the mechanical properties and porcelain bond strength of cobalt-chromium dental alloy fabricated by selective laser melting. *J Prosthet Dent*. 2014;111(1):51-55. doi:10.1016/j.prosdent.2013.09.011

20. Konieczny B, Szczesio-Wlodarczyk A, Sokolowski J, Bociong K. Challenges of Co-Cr Alloy Additive Manufacturing Methods in Dentistry-The Current State of Knowledge (Systematic Review). *Materials (Basel)*. 2020;13(16):3524. doi:10.3390/ma13163524

21. Lee WF, Wang JC, Hsu CY, Peng PW. Microstructure, mechanical properties, and retentive forces of cobalt-chromium removable partial denture frameworks fabricated by selective laser melting followed by heat treatment. *J Prosthet Dent*. 2022;127(1):115-121. doi:10.1016/j.prosdent.2020.06.038

22. Alageel O, Abdallah MN, Alsheghri A, Song J, Caron E, Tamimi F. Removable partial denture alloys processed by laser-sintering technique. *J Biomed Mater Res B Appl Biomater*. 2018;106(3):1174-1185. doi:10.1002/jbm.b.33929

23. Almufleh B, Emami E, Alageel O, et al. Patient satisfaction with laser-sintered removable partial dentures: A crossover pilot clinical trial. *J Prosthet Dent*. 2018;119(4):560-567.e1. doi:10.1016/j.prosdent.2017.04.021

24. Oliveira TT, Reis AC. Fabrication of dental implants by the additive manufacturing method: A systematic review. *J Prosthet Dent*. 2019;122(3):270-274. doi:10.1016/j.prosdent.2019.01.018

25. Revilla-León M, Özcan M. Additive Manufacturing Technologies Used for 3D Metal Printing in Dentistry. *Curr Oral Health Rep*. 2017;1(4):1–8. doi:10.1007/s40496-017-0152-0

26. Revilla-León M, Sadeghpour M, Özcan M. A Review of the Applications of Additive Manufacturing Technologies Used to Fabricate Metals in Implant Dentistry. *J Prosthodont*. 2020;29(7):579-593. doi:10.1111/jopr.13212

27. Kruth JP, Mercelis P, Vaerenbergh J, Froyen L, Rombouts M. Binding Mechanisms in Selective Laser Sintering and Selective Laser Melting. *Rapid Prototyp J.* 2005; 1(11):26–36. doi:10.1108/13552540510573365

28. Ahn DG. Direct metal additive manufacturing processes and their sustainable applications for green technology: A review. *International Journal of Precision Engineering and Manufacturing-Green Technology*. 2016;1(3):381–95. doi: 10.1007/s40684-016-0048-9

29. Krug KP, Knauber AW, Nothdurft FP. Fracture behavior of metal-ceramic fixed dental prostheses with frameworks from cast or a newly developed sintered cobalt-chromium alloy. *Clin Oral Investig*. 2015;19(2):401-411. doi:10.1007/s00784-014-1233-2

30. Al Jabbari YS, Koutsoukis T, Barmpagadaki X, Zinelis S. Metallurgical and interfacial characterization of PFM Co-Cr dental alloys fabricated via casting, milling or selective laser melting. *Dent Mater*. 2014;30(4):e79-e88. doi:10.1016/j.dental.2014.01.008

31. Kim H, Jang SH, Kim Y, Son J, Min BK, Kim KH, et al. Microstructures and Mechanical Properties of Co-Cr Dental Alloys Fabricated by Three CAD/CAM-Based Processing Techniques. Materials. 2016; 20(9):596. doi: 10.3390/ma9070596

32. Zhou Y, Li N, Yan J, Zeng Q. Comparative analysis of the microstructures and mechanical properties of Co-Cr dental alloys fabricated by different methods. *J Prosthet Dent*. 2018;120(4):617-623. doi:10.1016/j.prosdent.2017.11.015

33. Hong MH, Lee DH, Hanawa T, Kwon TY. Comparison of microstructures and mechanical properties of 3 cobalt-chromium alloys fabricated with soft metal milling technology. *J Prosthet Dent*. 2022;127(3):489-496. doi:10.1016/j.prosdent.2020.07.037

34. Okazaki Y, Ishino A, Higuchi S. Chemical, Physical, and Mechanical Properties and Microstructures of Laser-Sintered Co-25Cr-5Mo-5W (SP2) and W-Free Co-28Cr-6Mo Alloys for Dental Applications. *Materials (Basel)*. 2019;12(24):4039. doi:10.3390/ma12244039

35. Hong JK, Kim SK, Heo SJ, Koak JY. Mechanical Properties and Metal-Ceramic Bond Strength of Co-Cr Alloy Manufactured by Selective Laser Melting. *Materials (Basel)*. 2020;13(24):5745. Published 2020 Dec 16. doi:10.3390/ma13245745

36. Øilo M, Nesse H, Lundberg OJ, Gjerdet NR. Mechanical properties of cobalt-chromium 3-unit fixed dental prostheses fabricated by casting, milling, and additive manufacturing. *J Prosthet Dent*. 2018;120(1):156.e1-156.e7. doi:10.1016/j.prosdent.2017.12.007

37. Dolgov N, Dikova T, Dzhendov D, Pavlova D, Simov M. Mechanical Properties of Dental Co-Cr Alloys Fabricated via Casting and Selective Laser Melting. *International Journal Materials Science Non-Equilibrium Phase Transformations*. 2016;21:3–7

38. Qi J, Ma L, Gong P, Rainforth WM. Investigation of the wear transition in CoCrMo alloys after heat treatment to produce an HCP structure. *Wear*. 2023;518–519:204649. doi: 10.1016/j.wear.2023.204649

39. Aboulkhair NT, Simonelli M, Parry L, Ashcroft I, Tuck C, Hague R. 3D printing of Aluminium alloys: Additive Manufacturing of Aluminium alloys using selective laser melting. *Prog Mater Sci*. 2019;106:100578. doi: 10.1016/j.pmatsci.2019.100578

## TABLES

**TABLE 1.** Brand name, manufacturer, and element composition of each material used per group

| **Group** | **Brand Name** | **Manufacturer** | **Element composition (wt%) as per manufacturer** |
|---|---|---|---|
| CAST | Wironit | Bego, Quebec, Canada | Co: 63.0, Cr: 30.0, Mo:5.0, Si: 1.0, Mn: 1.0; C: <1.0 |
| CNC | Magnum Splendidum | MESA, Brescia, Italy | Co: 61.0, Cr: 28.0, W:8.5; Si: 1.5, Mn: <1.0, Fe: <1.0 |
| DMLS | Modelstar S Powder | Scheftner, Mainz, Germany | Co: 61.5, Cr: 28.5, Mo:6.0, Si: <1.0, Mn: <1.0, Fe: <1.0; C: <1.0 |

CAST, lost wax casting technique; CNC, computer numerical control milling; DMLS, direct metal laser sintering; Co, Cobalt; Cr, chromium; Mo, molybdenum; Si, silica; Mn, manganese; Fe, iron; C, carbon; wt%, weight percentage.

**TABLE 2.** Mean ± SEM mechanical properties and microhardness of CAST, CNC, and DMLS specimens.

| **Group** | **0.2% yield strength (MPa)** | **Tensile strength (MPa)** | **Elongation (%)** | **Elastic modulus (GPa)** | **Flexural strength (MPa)** | **Microhardness (HV)** |
|---|---|---|---|---|---|---|
| CAST | $462.1 \pm 8.0^{B}$ | $632.6 \pm 23.7^{B}$ | $2.3 \pm 0.2^{B}$ | $209.1 \pm 20.0^{A}$ | $1351.2 \pm 35.7^{B}$ | $400.0 \pm 33.3^{B}$ |
| CNC | $413.0 \pm 10.0^{C}$ | $533.1 \pm 17.4^{C}$ | $15.3 \pm 3.9^{A}$ | $192.5 \pm 15.2^{A}$ | $1155.6 \pm 41.7^{C}$ | $295.0 \pm 22.1^{C}$ |
| DMLS | $908.0 \pm 13.1^{A}$ | $1123.7 \pm 6.5^{A}$ | $10.1 \pm 0.6^{AB}$ | $227.4 \pm 6.2^{A}$ | $2273.0 \pm 43.2^{A}$ | $438.2 \pm 44.9^{A}$ |

CAST, lost wax casting technique; CNC, computer numerical control milling; DMLS, direct metal laser sintering. SEM, standard error of mean.

Different letters represent significant differences ($p < .05$) between groups.

**TABLE 3.** Results of quantitative elemental spot analysis with Energy Dispersive X-ray analysis (EDX)

| **Element composition (wt%)** | | | | | | | |
|---|---|---|---|---|---|---|---|
| **Group** | **Spot** | **Co** | **Cr** | **Mo** | **Mn** | **Si** | **W** |
| CAST | 1 | 62.7 | 30.3 | 4.5 | 1.6 | 0.8 | ND |
| | 2 | 62.8 | 30.2 | 4.5 | 1.6 | 0.9 | ND |
| | 3 | 62.7 | 30.3 | 4.4 | 1.7 | 0.9 | ND |
| | **mean (SD)** | **62.7 (0.05)** | **30.2 (0.05)** | **4.4 (0.05)** | **1.6 (0.05)** | **0.86 (0.05)** | **ND** |
| CNC | 1 | 62.4 | 27.8 | 0.2 | 1.2 | 1.5 | 6.8 |
| | 2 | 62.1 | 27.7 | 0.2 | 1.3 | 1.6 | 7.1 |
| | 3 | 61.9 | 28.1 | ND | 1.4 | 1.5 | 7.1 |
| | **mean (SD)** | **62.1 (0.25)** | **27.8 (0.20)** | **0.2 (0)** | **1.3 (0.1)** | **1.5 (0.05)** | **7.0 (0.17)** |
| DMLS | 1 | 64.0 | 29.4 | 4.3 | 1.8 | 0.6 | ND |
| | 2 | 63.7 | 29.3 | 4.4 | 1.8 | 0.8 | ND |
| | 3 | 64.1 | 29.1 | 4.4 | 1.6 | 0.7 | ND |
| | **mean (SD)** | **63.9 (0.2)** | **29.2 (0.15)** | **4.3 (0.05)** | **1.7 (0.11)** | **0.7(0.1)** | **ND** |

CAST, lost wax casting technique; CNC, computer numerical control milling; DMLS, direct metal laser sintering; Co, Cobalt; Cr, chromium; Mo, molybdenum; Mn, manganese; Si, silica; W, tungsten; wt%, weight percentage; ND, not detected.

**TABLE 4.** Mechanical properties by type specified in ISO 22674

| Type | 0.2% yield strength (MPa) | Elongation (%) | Elastic Modulus (GPa) |
|---|---|---|---|
| 0 | - | - | - |
| 1 | 80 | 18 | - |
| 2 | 180 | 10 | - |
| 3 | 270 | 5 | - |
| 4 | 360 | 2 | - |
| 5 | 500 | 2 | 150 |

## FIGURES

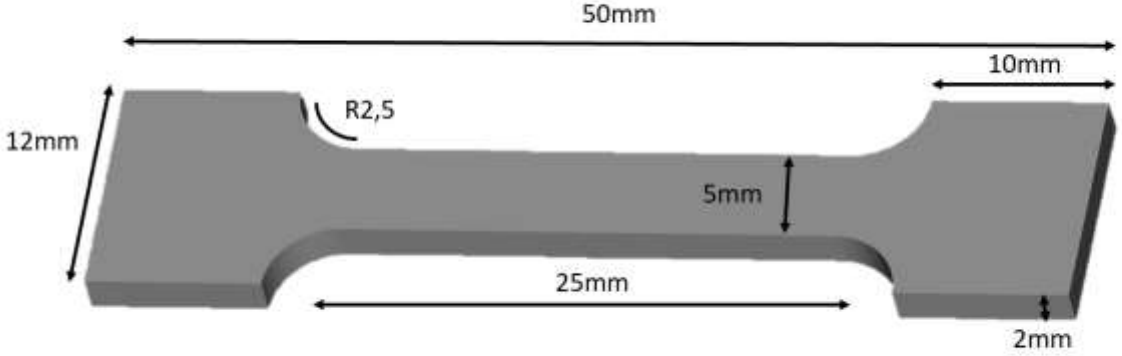

**Figure 1.** Specimen dimensions according to ISO 22674.

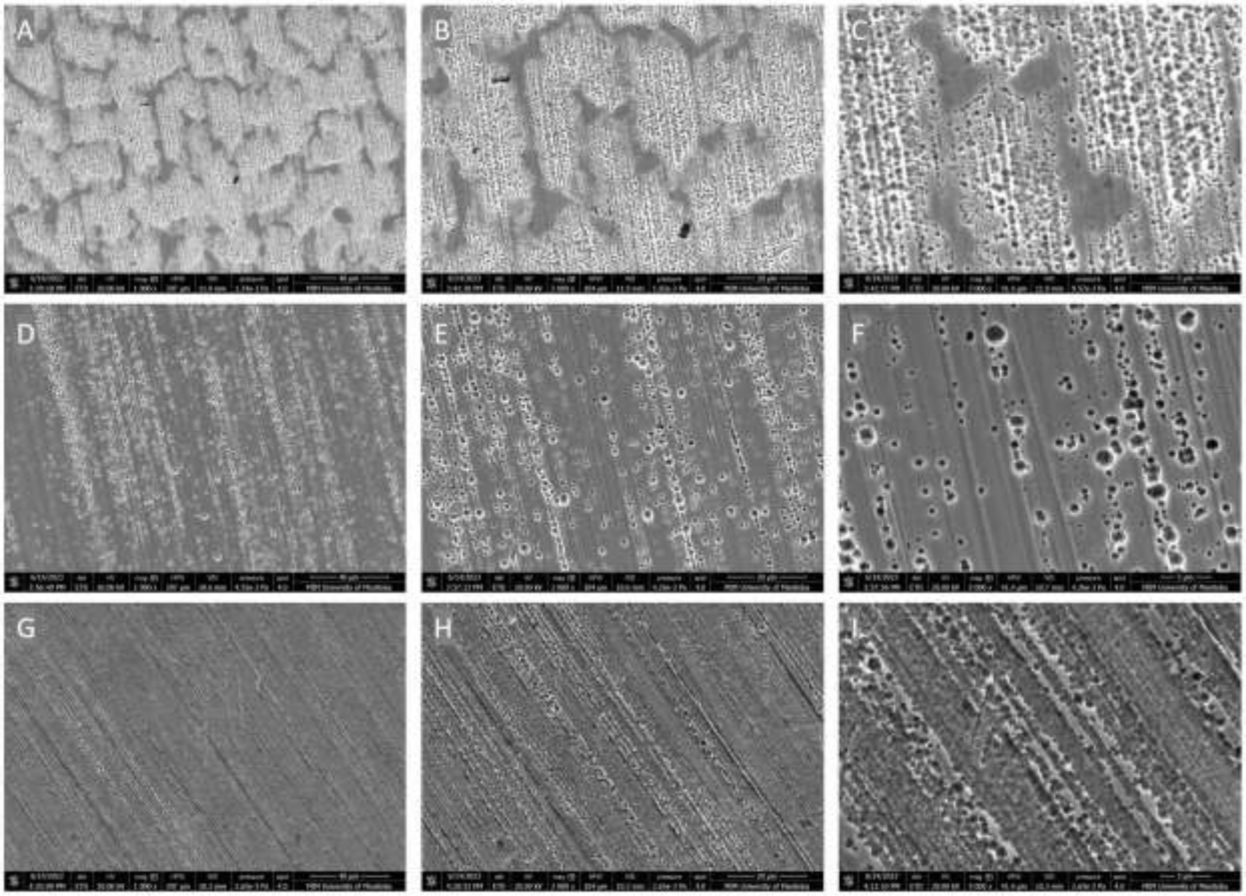

**Figure 2.** Representative scanning electron microscopy (SEM) of each tested group. A, B, C, CAST; D, E, F, CNC; G, H, I; DMLS. Original magnification A, D, G, x1000. Original magnification B, E, H, x2000. Original magnification C, F, I, x5000. CAST, lost wax casting technique; CNC, computer numerical control milling; DMLS, direct metal laser sintering.

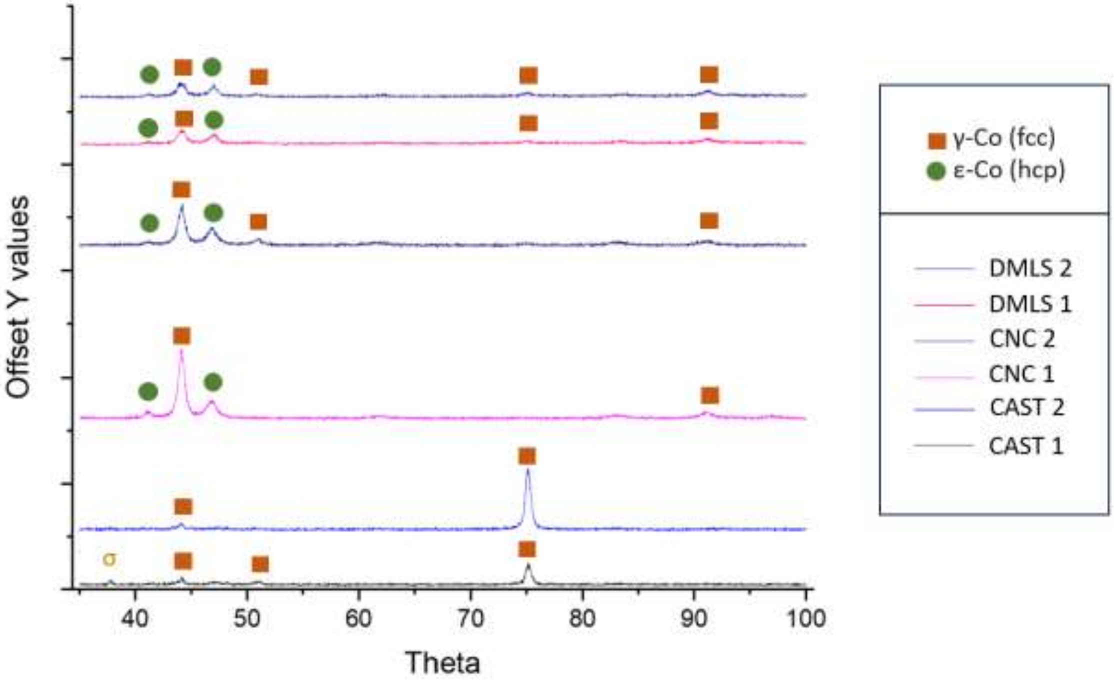

**Figure 3.** XRD spectra of the tested Co-Cr alloys. CAST, lost wax casting technique; CNC, computer numerical control milling; DMLS, direct metal laser sintering; XRD, X-ray diffraction.