

**COMPARATIVE EVALUATION OF CORROSION  
BEHAVIOR OF CONVENTIONAL AND DIRECT  
METAL LASER SINTERED (DMLS) Co-Cr DENTAL  
ALLOYS IN FLUORIDE SOLUTION  
-AN *IN VITRO* STUDY**

*Dissertation submitted to*

**MAHARASHTRA UNIVERSITY OF HEALTH SCIENCES,  
NASHIK**

*In the partial fulfilment of regulations*

*for the award of the degree of*

**MDS**

**IN**

**PROSTHODONTICS INCLUDING REMOVABLE, FIXED,  
MAXILLOFACIAL AND IMPLANTOLOGY**

**BRANCH -I**

**2018**

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<b>SR NO.</b>	<b>ABBREVIATIONS</b>	<b>FULL FORM</b>
1.	Co-Cr	Cobalt- Chromium
2.	DMLS	Direct Metal Laser Sintering
3.	STL	Stereo lithography
4.	SLI	Slice Layer Interface
5.	AM	Additive manufacturing
6.	EOS	E-manufacturing solutions
7.	PDP	Potentiodynamic polarization
8.	EIS	Electrochemical impedance spectroscopy
9.	$I_{\text{corr}}$	Corrosion current density
10.	$E_{\text{corr}}$	Corrosion potential
11.	Sr. no.	Serial number
12.	SD	Standard deviation
13.	EC	Electrochemical
14.	Gm	Grams
15.	Div	Division
16.	OCP	Open circuit potential
17.	EIS	Electrochemical impedance spectroscopy
18.	mV	Millivolt
19.	$\mu\text{A}/\text{cm}^2$	Unit for corrosion current density
20.	EC	Electrochemical

# *Introduction*

*The key to growth is the introduction of higher dimensions of consciousness into  
our awareness*

The field of dental materials is highly catholic in nature, in the sense it covers a wide variety of materials from fairly exotic resin systems, elastomers, metals, alloys to ceramic materials and many others. Metals and its alloys have been used as substitute materials for missing tooth tissues for thousands of years. The non-precious alloys are rapidly coming in vogue replacing precious or noble alloys in dentistry. The safe use of these alloys depends on factors such as biocompatibility, corrosion behavior, mechanical properties, fabricability, cost, availability, aesthetics etc.<sup>1, 2, 3</sup>

The most important feature required for these dental alloys is to be biocompatible before exhibiting necessary physical and mechanical properties so as to ensure patient safety, adequate function and durability when they come in contact with oral tissues and biting forces. However, dental alloys are also exposed daily to different conditions in the oral cavity which offer ideal conditions for corrosion and chemical degradation of most dental materials. Therefore, it becomes important to investigate the corrosion behavior of these dental alloys to evaluate its biocompatibility in clinical use.<sup>4,5,6</sup>

The Co-Cr alloys have attracted great attention in the past decades for the fabrication of removable partial denture frameworks and fixed prosthesis because of their low cost, high strength and rigidity, low density and good corrosion resistance. However, the use of these alloys is limited by their susceptibility to corrosion in the biological environment, since corrosion products can be toxic and allergic.<sup>7,8</sup>

The corrosion resistance of dental alloys in the biological environment depends on several factors such as alloy composition, nature of elements, microstructural phases and inclusions, solace condition of the metal or alloy, composition and chemical characteristics of the corrosive solution, temperature, movement or circulation of the medium in contact with an alloy surface, passivation, casting and finishing procedures.<sup>9</sup>

Over the past decades, these metallic restorations were typically produced by using the lost-wax casting technique. However, in these casting techniques, casting imperfections such as porosities or impurities due to the presence of corrosion-prone mixed crystals can impair the quality of the casting. To overcome these limitations, new techniques have been introduced.<sup>10</sup>

With the extensive advancement of computer-aided technologies in dentistry, there is significant scope to replace the traditional casting technique with layer manufacturing techniques such as Additive Manufacturing (AM) in complex intra-oral framework production. One of the recently introduced techniques based on AM system is Direct Metal Laser Sintering (DMLS) that fabricates restorations by applying a laser, which selectively melts a metal powder to build up layers of a solidified material.<sup>8, 11</sup>

Laser sintering process was first introduced by Deckard and Beaman. Unlike cast denture frameworks which are manufactured by the 'lost wax' process, DMLS is a manufacturing process for producing complex 3D components directly from 3D CAD data without using any machining. DMLS requires three inputs: material, energy and CAD model. The material used is powder-based working material. DMLS crowns have a primary composition of chrome cobalt alloy.<sup>12</sup> It is a one-step process that fabricates the metal parts through layer-wise material addition techniques, allowing the operator to generate solid frameworks by selectively consolidating successive layers of powder materials on top of each other, using thermal energy supplied by a focused and computer-controlled laser beam. Hence the steps such as waxing, investing, and casting procedures are eliminated, thus preventing the distortion of frameworks and avoiding faults by the clinician and dental technician, and the working time is significantly reduced. However, the high cost of the equipment is a disadvantage of this technique.<sup>8, 13, 14</sup>

The oral cavity is considered to be a rigorous medium that promotes the corrosion of dental alloys. It is wet and it is continually exposed to temperature

fluctuations. Foods and beverages cause important changes in environmental chemistry. The food and fluid ingested have wide ranges of pH. Acids are released during the decomposition of foodstuffs. Food remains often adhere tenaciously to metal restorations providing a localized condition favoring an accelerated reaction between oral media and metal or alloy.<sup>15</sup>

Oral treatments with fluoride are recognized as an effective method of preventing dental caries. A lot of commercially available products such as toothpastes and mouthwashes have Sodium fluoride (NaF) content. Many studies have proven the degradation of Titanium alloys due to the use of fluoride.<sup>16, 17</sup> However, the effect fluoride on the corrosion behavior of Co-Cr alloys fabricated by different manufacturing methods i.e. traditional casting and DMLS technology has not been investigated yet.

Therefore, the purpose of the present study is to investigate the electrochemical corrosion behavior of Co-Cr alloys produced by casting and DMLS methods in a medium simulating the oral environment.

The null hypothesis formulated was that ‘both the fluoride concentration and manufacturing methods (cast and DMLS) will have no influence on the corrosion behavior of Co-Cr alloys.’

The alternate hypothesis formulated was that ‘both the fluoride concentration and manufacturing methods (cast and DMLS) will have a significant influence on the corrosion behavior of Co-Cr alloys.’

# *Aim and Objectives*

*We aim above the mark to hit the mark*

*In whatever position you find yourself, determine first your objective*

## **AIM**

To evaluate and compare the corrosion rate of Conventional and Direct Metal Laser Sintered (DMLS) Co-Cr dental alloys in fluoride solution

**OBJECTIVES**

1. To evaluate the corrosion rate of Conventional Co-Cr dental alloys in fluoride solution.
2. To evaluate the corrosion rate of Direct Metal Laser Sintered (DMLS) Co-Cr dental alloys in fluoride solution.
3. To compare the corrosion rate of Conventional and Direct Metal Laser Sintered (DMLS) Co-Cr dental alloys in fluoride solution.

# *Review of Literature*

*Review your goals twice everyday in order to be focused on achieving them*

**Rechmann P (1993)<sup>18</sup>** identified metallic components and microparticles from cast metal restorations in clinically healthy gingival tissues.

**Rechmann P, von Bohlen A and Tourmann JL (1994)<sup>19</sup>** identified metallic components and microparticles from cast metal restorations in microbial plaque.

**Reclaru L and Meyer JM (1998)<sup>20</sup>** evaluated the effect of fluoride ions on titanium and dental alloys used for dental implants and superstructures. Two different milieus based on the Fusayama artificial saliva and an electrolyte solution containing NaCl, with and without fluoride ions, were used for the electrochemical tests, in a pH range of 6.15 to 3.0. Electrochemical procedures i.e. Open circuit potentials (OCP), Potentiodynamic curves (PDP), Tafel slopes, Galvanic couplings and Crevice potentials were performed and it was concluded that;

(a) With and without fluoride ions, galvanic currents are weak ( $10E^{-7}$  to  $10E^{-8}$  A  $cm^{-2}$ ) within a pH range of 6.15 to 3.5;

(b) Titanium submitted to anodic polarization in an electrolyte, even one containing fluoride, merely develops an oxide layer and does not corrode within that same pH range of 6.15 to 3.5;

(c) In confined areas where fluoride ions are present, titanium and the dental alloys tested undergo a corrosive process, in the form of crevice and pitting, as soon as the pH drops below 3.5.

**Khan MA, Williams RL, Williams DF (1999)**<sup>21</sup> studied and compared the *in vitro* corrosion of three Ti alloys in various protein solutions with phosphate-buffered saline (PBS = control) at different pHs (5, 7.4 and 9) and concluded that corrosion in PBS was higher at low pH.

**Kaneko T, Hattori M, Hasegawa K, Yoshinari M, Kawada E and Oda Y (2000)**<sup>22</sup> studied and compared the influence of finishing on the electrochemical properties of precious-metal alloys with that of base-metal alloys. Three types of finishing procedure were examined i.e. mirror-finishing using 0.05-micron alumina particles, polishing up to #600 abrasive paper and sandblasting. Electrochemical properties such as; Polarization resistance ( $R_p$ ) and Potentiodynamic polarization (PDP) were measured in 0.9% NaCl solution. It was found that the corrosion properties were improved in the order of sandblasting, #600-abrasive-paper polishing, and mirror-finishing. It was concluded that finishing affected the electrochemical measurement of dental alloys and mirror-finished specimens can be recommended for use in evaluation and comparison of the corrosion resistance of various dental alloys.

**Hanawa T, Hiromoto S and Asami K (2001)**<sup>23</sup> studied the surface oxide films on a Co–Cr–Mo alloy located in various environments to estimate composition, substrate and thickness of the film in the human body using X-ray photoelectron spectroscopy (XPS) analysis. Five kinds of specimens were prepared according to the following methods: polishing in deionized water, autoclaving, immersion in Hanks' solution, immersion in a cell culture medium, and incubation with cultured cells. It was found that the surface oxide film was about 2.5 nm thick and contained a large amount of  $\text{OH}^-$ . Calcium phosphate was formed and Cobalt was dissolved after immersion in the Hanks' solution, the culture medium and incubation with the cultured cells. After the dissolution, the surface oxide consisted of chromium oxide ( $\text{Cr}^{3+}$ ) containing molybdenum oxide ( $\text{Mo}^{4+}$ ,  $\text{Mo}^{5+}$ , and  $\text{Mo}^{6+}$ ). Results from angle-resolved XPS revealed that chromium and molybdenum were more widely distributed in the inner layer than in the outer layer of the oxide film. It was concluded that Co–Cr–Mo alloy releases cobalt and that the surface oxide film consisting of chromium and molybdenum is reconstructed in living tissues.

**Schmalz G and Garhammer P (2002)**<sup>24</sup> in a literature survey described the interactions of dental cast alloys with living tissues and related them to clinically adverse local reactions of the oral tissues. It was observed that these alloys can cause local tissue responses, such as gingivitis and periodontitis in the oral cavity.

**Huang HH (2003)**<sup>25</sup> studied the effect of fluoride and albumin concentration on the corrosion behavior of Ti–6Al–4V alloy in acid artificial saliva (pH 5/37°C) using PDP and linear polarization test. It was found that the presence of NaF led to higher  $I_{\text{corr}}$  and  $I_{\text{pass}}$ ; and lower  $R_p$ ; especially when NaF concentration was  $\geq 0.15\%$ .

The addition of albumin (0.01–0.2%), regardless of the concentration, to the fluoride-containing media considerably improved the corrosion resistance. The protectiveness of the TiO<sub>2</sub> passive film formed on Ti–6Al–4V alloy was destroyed by fluoride ions via the formation of Na<sub>2</sub>TiF<sub>6</sub> when the NaF concentration was increased up to 0.1%. It was concluded that, increasing the NaF concentration (0.01–0.5%) led to a decrease in the corrosion resistance.

**Knezović-Zlaticar D, Nemet M and Baucic I (2003)<sup>26</sup>** discussed the laboratory fabrication procedures of a metal partial denture framework. It was reviewed that the alloy used for fabrication of metal partial dentures consists mainly of Co (62-65%), Cr (23-31%) and Mo (4.5-5.5%). Cobalt in the alloy enhances good mechanical properties and reduces the viscosity of the alloy, chromium improves the chemical stability of the alloy and its stability in the mouth, while molybdenum increases the chemical stability of the alloy and bonds with the excess of unburned carbon (increasing the brittleness of the alloy), creating molybdenum-carbide (Mo<sub>6</sub>C).

**Kumar S (2003)<sup>27</sup>** overviewed the selective laser sintering (SLS) work and concluded that with the advent of proprietary processes and materials for sintering and extensive research on various aspects of the process; SLS has established itself as a reliable means for rapid prototyping and is rapidly emerging as a technique for rapid manufacturing. However, comparatively little work has been done in computational modeling for the SLS of metals and alloys, and most of the experimental works executed are commercial machine-specific.

**Rincić N, Bačić I, Miko S, Papić M and Prohić E (2003)<sup>28</sup>** studied the corrosion behavior of the Co-Cr-Mo dental alloy (WIRONIT<sup>R</sup>, BEGO, Germany) in

solutions of different compositions and different pH values over a relatively long period of time. Co-Cr-Mo dental alloy was exposed to simulated saliva (phosphate buffer pH 6.0), a highly acidic medium resembling the extreme conditions in the oral cavity (phosphate buffer pH 3.5), and in lactic acid at pH which occurs under the dental plaque (lactic acid pH 3.5). Six samples of each alloy were immersed in each of these three solutions for 1, 2, 3, 4, 5, 6, 7, 14, 21, and 30 days, i.e. a total of 180 samples were tested. Solutions were analyzed with the ICP-AES. The analysis showed that during one-month cobalt (Co), chromium (Cr), iron (Fe), zinc (Zn) and nickel (Ni) ions had been released from tested samples in all three solutions. It was concluded that the leaching of the Co, Cr, Fe, Zn and Ni ions in the solution was dependent both upon the nature of the solution in which the alloy was immersed and the duration of the immersion.

**Rincić N, Celebić A, Baucić I, Stipetić J, Prohić E and Miko S (2003)<sup>5</sup>** studied the release of ions from the base Co-Cr-Mo casting alloy (WIRONIT<sup>R</sup>) into the Phosphate Buffer at pH 6.0 over a relatively long period of time and also determined the influence of the time period, during which the casting alloy was exposed to the phosphate buffer at pH 6.0. The release of ions was measured on ten occasions: 1, 2, 3, 4, 5, 6, 7, 14, 21 and 30 days. An analysis of the solution into which samples of the tested alloy were plunged, showed that cobalt (Co), chromium (Cr), iron (Fe), zinc (Zn) and nickel (Ni) ions were released during the month. Co ions were released from the base Co-Cr-Mo alloy in the greatest amount while Fe ions were released in the smallest amount. It was concluded that the time of exposure to the phosphate buffer at pH 6.0 had statistically significant influence ( $p < 0.01$ ) in the release of all detected ions from the Co-Cr-Mo alloy.

**Ameer MA, Khamis E and Al-Motlaq M (2004)**<sup>29</sup> studied the corrosion behavior of dental alloys in artificial saliva using different chemical and electrochemical techniques. The results of ICP-MS indicated that Fe, Co, Cr and Ni are the most soluble ions in artificial saliva. It was found that, increasing scan rate leads to an increase in the critical current ( $I_{cc}$ ). The corrosion resistance of the three non-precious alloys was observed in the following order: wironit > wirolloy > wiron99. The open-circuit potential of wirolloy was more positive than wiron99. It was concluded that, the studied non-precious alloys had a high corrosion resistance and Co–Cr–Mo alloy exceeds corrosion resistance than that of the other alloys containing Ni–Cr–Mo in artificial saliva. It was also concluded that the scan rate of 10 mV/min is the best scan rate because at this value the corrosion rate is very low when compared at 50 mV/min.

**Giacomelli FC, Giacomelli C and Spinelli A (2004)**<sup>30</sup> studied the corrosion behavior of a Co-Cr-Mo biomaterial used as dental prosthesis by electrochemical (OCP and PDP) and surface analysis techniques (SEM and EDS) in artificial saliva, artificial saliva with modified temperature (7 °C – 47 °C) and pH (1.4 – 13.4), and containing fluoride (1500 ppm). The results revealed that the surface morphology after PDP is highly heterogeneous exhibiting three regions of different composition. Soluble metal species such as  $CrO_4^{2-}$  were released to the solution during the PDP. It was concluded that the electrochemical processes were markedly influenced by solution temperature and pH, whereas the presence of fluoride did not produce changes in the system.

**Kocijan A, Milošev I and Pihlar B (2004)**<sup>31</sup> studied the composition of the passive layers of Cobalt-based (Co–Cr–Mo and Co–Ni–Cr–Mo) alloys used for orthopaedic applications using electrochemical and XPS analysis in simulated physiological solution (SPS), with and without the complex agent EDTA. It was found that Chromium oxide was the major constituent of the passive layer on both Co–Cr–Mo and Co–Ni–Cr–Mo alloys. The minor constituents of the passive layers, Co- & Mo- oxide in the case of Co–Cr–Mo alloy and Ni-, Co- and Mo-oxides in the case of Co–Ni–Cr–Mo alloy, are also located in the outer part of the layer. It was concluded that, EDTA affects the formation of the passive layer on each alloy. Also, the content of Co-, Ni- and Mo-oxide in the passive layer was lower in the presence of EDTA.

**Hsu RW, Yang CC, Huang CA and Chen YS (2005)**<sup>32</sup> studied the corrosion behavior of Co–Cr–Mo implant alloys in different biological solutions including urine, serum and joint fluid using PDP, Cyclic voltammetry (CV), and ac impedance spectroscopy. The corrosion characteristic properties of Co–Cr–Mo implant alloys were investigated in terms of corrosion potential ( $E_{\text{corr}}$ ), corrosion current density ( $I_{\text{corr}}$ ), and ac polarization resistance ( $R_p$ ). It was found that the Co–Cr–Mo implant alloy exhibits small passive region in joint fluid and serum. The corrosion resistance of Co–Cr–Mo implant alloys in urine was lower than that in joint fluid and serum at  $E_{\text{corr}}$  and 37 °C. The corrosion current densities ( $I_{\text{corr}}$ ) of Co–Cr–Mo implant alloys in three biological solutions were within a range of 1.65–2.59  $\mu\text{Acm}^{-2}$ . The ac circuit parameters for corrosion interface of Co–Cr–Mo alloy in biological solutions were calculated based on the simple Randle model. It was concluded that the ac model predictions were in good agreement with the experimental results.

**Kwon YH, Seol HJ, Kim HI, Hwang KJ, Lee SG, Kim KH (2005)**<sup>17</sup> studied the interaction between acidic fluoride solution and  $\beta$  titanium alloy to explore the changes that occur in the alloy by fluoride-containing acetic acid solutions. The alloy crystal structure, tensile strength, and elements released from the alloy wires were determined using four solutions (0.05%/pH 6, 0.05%/pH 4, 0.2%/pH 6, and 0.2%/pH 4) for 1 or 3 days. It was found that the immersed wire did not form any identifiable new crystal structure compared with the as-received wire. The tensile strength of the immersed wires was significantly reduced compared to the as-received wires in the test solutions if the period of immersion increased from as-received to 3 days. The fractured area of the immersed wire was reduced compared to the as-received one. It was also observed that after a 3-day immersion, the amount of the released Ti and Mo had much increased for higher NaF concentration and lower pH value. It was concluded that during the long-period orthodontic treatment, both patient and the clinical doctor should carefully use the fluoride-containing products to minimize unexpected damage on orthodontic wires.

**Mareci D, Nemtoi G, Aelenei N and Bocanu C (2005)**<sup>33</sup> evaluated the electrochemical behavior of various non-precious Ni- and Co- based alloys in artificial saliva and found that the Vitallium, Wiroloy and Wiron NT alloys showed a strong corrosion resistance. It was observed that high chromium and molybdenum content in an alloy exhibited a much wider passivation range and a better resistance to pitting corrosion. Also, the corrosion current values decreased with the maintenance time due to their passivation in solution. It was concluded that the chromium and molybdenum contents played a significant role in corrosion resistance and the maintenance times of the alloy in the corrosive medium influenced the corrosion rate.

**Mehulic K, Mehulic M and Kos P (2005)**<sup>34</sup> summarized the contact sensitivity reactions to dental alloys. It was found that restorations are in long-term direct contact with oral tissues & saliva; and during function they wear and bend, leading to corrosive processes which result in the release of ions, their accumulation in the tissues and possible sensitivity, i.e. allergic reaction.

**Mehulić M, Mehulić K, Kos P, Komar D and Katunarić M (2005)**<sup>35</sup> examined the occurrence of allergies to basic and auxiliary restorative dental materials in patients with lichen, stomatitis and stomatopyrosis by means of an epicutaneous allergy test. 32 patients with a fixed and/or removable replacement and 7 patients with one of the mentioned diagnoses, but without any replacement were enrolled in the study. The results revealed higher frequency of positive allergic reactions in persons with the mentioned diseases and with a restoration. Patients with lichen indicated positive patch test in the majority of cases. The allergens of nickel, cobalt and chromium demonstrated the highest score of positive results, and the negative score was found for dibutyl phthalate and HH mix. Stomatopyrosis was more common in persons with hypersensitivity to chromium. A lower incidence of positive allergic reactions to epoxide resins was found in female than in male subjects. It was concluded that the majority of positive reactions were caused by mixes of nickel, cobalt and chromium.

**Reclaru L, Lüthy H, Eschler PY, Blatter A and Susz C (2005)**<sup>36</sup> studied the corrosion behavior of four commercial dental Co-Cr alloys doped with different proportions of precious metals. These alloys with different doping levels were tested by the electrochemical techniques in two different milieus based on the Fusayama

artificial saliva and an electrolyte containing NaCl. The results showed that the presence of precious metals can deteriorate the corrosion behavior of Co-Cr alloys in a significant way. Gold/Platinum doping, in particular, produced heterogeneous microstructures that are vulnerable to corrosive attack. It was concluded that Co-Cr dental alloys doped with precious metals do not provide a valuable improvement with respect to conventional Co-Cr alloys.

**Viennot S, Dalard F, Lissac M and Grosogeat B (2005)<sup>37</sup>** assessed and compared the corrosion behavior of one Co-Cr (Duceralloy U; Degudent) and two Pd-Ag (Degudent, Hanau-Wolfgang, Germany and Qualident, Geneva, Switzerland) alloys used in FPD's. It was observed that, the corrosion potential of the Co-Cr alloy was lower than that of the Pd-based alloys, the corrosion currents and polarization resistance values were similar for all three alloys. All materials showed a very high resistance to corrosion. It was concluded that the three experimental alloys exhibit corrosion resistance compatible with their use in the manufacture of dental prostheses. The Co-Cr alloy can be used as a suitable alternative to Pd-Ag for use in the manufacture of fixed dental prostheses.

**Viennot S, Lissac M, Malquarti G, Dalard F and Grosogeat B (2006)<sup>6</sup>** studied and compared the in vitro corrosion resistance in artificial saliva of two Pd-Ag alloys (Pors on 4) and an Ag-Pd (Palliag LTG), with and without casting defects; 1 nickel-chrome alloy and 1 high-gold alloy, casted under recommended conditions were used as controls. For each of the Pd-based alloys, three specimens corresponding to three different casting conditions were used: under recommended conditions, with the use of a graphite-containing investment and crucible, and by

reusing the sprues and sprue button. After recording the OCP, the PDP was performed to measure the polarization resistance ( $R_p$ ) and the corrosion current ( $I_{\text{corr}}$ ). Further, each specimen was examined by SEM analysis. In comparison to the control alloys, the electrochemical experiments in artificial saliva indicated satisfactory corrosion resistance for the Pd–Ag and Ag–Pd alloys; due to their high noble metal content and stable substructure. The Pd–Ag alloy displayed superior electrochemical properties to those of the Ag–Pd alloy regardless of the casting condition. It was found that the use of the graphite-containing crucible and investment during the cast process did not dramatically reduce the corrosion resistance values, but the reuse of sprues and the sprue button did.

**Bilhan H, Bilgin T, Cakir AF, Yuksel B and Von Fraunhofer JA (2007)**<sup>38</sup> studied the relationship of organic constituents of saliva (IgA, mucine, urea, and lysozyme) and the corrosion of dental alloys (titanium, Co–Cr–Mo and Ni–Cr–Mo alloys, and dental amalgam). The results showed that Ni–Cr–Mo and dental amalgam alloys were highly susceptible to corrosion in all the investigated media. The Co–Cr–Mo alloy had shown high passive current densities ( $I_{\text{pass}}$ ) in the solution of mucine and lysozyme in artificial saliva. Titanium showed a high resistance to corrosion and a stable passive behavior in all media, especially in a solution of mucine and IgA in synthetic saliva. Mucine and IgA, as well as urea and lysozyme, appeared to enhance the formation of a passive film layer on the Ti metal surface, inhibiting the corrosion. After considering the problem of nickel allergy and toxicity of mercury released from dental amalgam it was concluded that the use of Co–Cr–Mo alloys and Ti to Ni–Cr–Mo alloys is recommended and alternatives to dental amalgam should be sought for patients with the impaired salivary flow.

**Sharma M, Ramesh Kumar AV, Singh N, Adya N and Saluja B (2008)**<sup>3</sup> evaluated the corrosion behavior and passive film characteristics of various dental alloys such as Co-Cr, Ni-Cr, Cu-Ni-Al and commercially pure Ti (cp Ti) in artificial saliva medium utilizing electrochemical impedance spectroscopy (EIS), Tafel polarization, and cyclic polarization studies. EIS studies were carried out for various durations viz. 1 h, 1 day, and 7 days to evaluate the stability of passive film and change in corrosion characteristics with respect to time. Electrochemical parameters such as  $E_{\text{corr}}$ ,  $I_{\text{corr}}$ , corrosion rate, passive film characteristics with respect to time were also obtained. It was found that the corrosion resistance decreased in the order Cu-Ni-Al > cp Ti > Co-Cr (Commercial) > Ni-Cr > Co-Cr (DRDO developed) in artificial saliva solution.

**Songur M, Celikkan H, Gokmese F, Simsek SA, Altun NS and Aksu ML (2009)**<sup>39</sup> studied the corrosion behavior of 316 stainless steel, Co-Cr-Mo and Ti6Al4V alloys in simulated body conditions (ringer lactate) at 37°C by the use of Tafel plots, mixed potential and electrochemical impedance spectroscopy (EIS). It was found that Ti6Al4V alloy has the highest corrosion resistance followed by Co-Cr-Mo alloy. It was concluded that Ti6Al4V was the most suitable material for implant applications in the human body. In addition to titanium alloy, Co-Cr-Mo alloy also has a significant corrosion resistance in biological media. Due to its comparable strength and cost-effectiveness Co-Cr-Mo alloy can also be a good alternative as an implant material.

**Sun D, Wharton JA and Wood RJ (2009)**<sup>40</sup> assessed the tribo-corrosion behavior of cast Co-Cr-Mo (F-75) under various abrasion–corrosion conditions by

using a modified microabrasion tester incorporating a three-electrode electrochemical cell. The effects of reduced abrasive size/ hardness and volume concentration, as well as the role of proteins on the tribo-corrosion performance of the cast Co-Cr-Mo alloy, were addressed. It was concluded that the reduction in abrasive size and volume concentration can significantly affect the abrasion–corrosion wear mechanisms and the wear-induced corrosion response of the material.

**Sun D, Wharton JA, Wood RJK, Ma L and Rainforth WM (2009)**<sup>41</sup> investigated the sliding corrosion and abrasion–corrosion performance of a cast Co-Cr-Mo alloy in simulated hip joint environments using a microabrasion rig integrated with an electrochemical cell in 0.9% NaCl, phosphate buffered saline solution, 25% and 50% bovine serum solutions with 0 or 1 g cm<sup>-3</sup> SiC at 37°C. The results revealed that under abrasion–corrosion test conditions, the presence of proteins increased the corrosion rate. Conversely, the electrochemical noise measurements indicated that the average anodic current levels were appreciably lower for the proteinaceous solutions when compared with the inorganic solutions. A severely deformed nanocrystalline layer was identified immediately below the worn surface for both proteinaceous and inorganic solutions by a recrystallization process and/ or a strain-induced phase transformation that occurs during microabrasion corrosion. It was also observed that minor variations in test solution chemistries can significantly influence to wear-corrosion behavior of the cast Co-Cr-Mo alloy.

**Tuna SH, Pekmez NÖ, Keyf F and Canli F (2009)**<sup>42</sup> investigated the electrochemical properties (PDP and OCP) of four dental casting (Co-Ni based, Co-Cr based, Pd based and Au based) suprastructure alloys coupled with titanium implant in

Afnor type artificial saliva solution at 37°C. It was concluded that the titanium implant forms a stable passive oxide layer in artificial saliva exposed to open air and it does not affect the corrosion properties of the suprastructures. The Au- and Pd-based, noble alloys were more corrosion-resistant than base alloy couples.

**Tuna SH, Pekmez NÖ, Keyf F and Canli F (2009)<sup>2</sup>** studied the influence of pure metal components of four different casting alloys on the corrosion behaviors of these alloys. It was found that Ni–Cr (M1) and Co–Cr (M2) alloys had a more homogenous structure than palladium based (M3) and gold based (M4) alloys. It was also found that the total ion concentration released from noble metal-based alloys was less than that of base metal alloys. It was also observed, that the noble metals in the M3 and M4 samples decreased the current density in the anodic branch of the PDP curves. It was concluded that casting alloys containing gold are preferable in the oral cavity despite of their heterogeneous structure.

**Mareci D, Cailean A, Ciurescu G and Sutiman D (2010)<sup>43</sup>** studied the electrochemical properties (PDP and EIS) of four Ni-Cr alloys (Wirrolloy, Heraenium, NicromalSoft and VeraSoft) after maintaining in a 0.1M NaCl solution for 1 min, 1 hour and 24 hours. The results of EIS showed that all NiCr-based alloys exhibit passivity at open circuit potential. It was observed corrosion current values all the samples decreased with the increase of the immersion time. The alloys Heraenium and Wirrolloy were in the optimum corrosion resistant condition. The VeraSoft and NicromalSoft alloys presented a dangerous breakdown potential (about 200-300 mV). It was concluded that Heraenium alloy with high Cr & Mo content and dendrite microstructure exhibit a much wider passivation range and therefore showed the best

electrochemical behavior in 0.1M NaCl solutions. Also, the polarization resistance increases with the immersion time.

**Mareci D, Sutiman D, Cailean A and Bolat G (2010)**<sup>44</sup> studied the electrochemical behavior (PDP and EIS) of two Ag–Pd alloys (Unique White and Paliag) used in the fabrication of crowns and bridges and one Co–Cr alloy (Vitallium 2000) in artificial saliva. It was found that these alloys somewhat had a good corrosion resistance in artificial saliva. The corrosion current densities of Unique White and Vitallium 2000 alloys were very low (~100 nA/cm<sup>2</sup>). The passivation of all samples occurred spontaneously at the open circuit potential. The polarization resistance ( $R_p$ ) of all the samples increased with the immersion time and was largest for Unique White (Ag–Pd) and Vitallium 2000 (Co–Cr) alloys. It was concluded that the Co–Cr alloy exhibit excellent corrosion resistance and can be used as an alternative to Ag–Pd alloys to make fixed prosthetic elements.

**Anwar EM, Kheiralla LS and Tammam RH (2011)**<sup>45</sup> studied the effect of fluoride ion concentration on the corrosion behavior of Ti and Ti6Al4V implant alloys, when coupled with either metal-ceramic or all-ceramic superstructure, using electrochemical methods in artificial saliva solutions. It was found that fluoride ion concentrations higher than 0.1 M greatly affected Ti6Al4V couples compared to commercially pure Ti couples. It was concluded that increased fluoride concentration leads to a decrease in the corrosion resistance of all tested couples.

**Igual Muñoz A and Mischler S (2011)**<sup>46</sup> studied the corrosion behavior and the wear ranking of biomedical high carbon (HC) and low carbon (LC) Co-Cr-Mo alloys sliding against an alumina ball in four different simulated body fluids [NaCl

and phosphate buffered solutions (PBS) with and without albumin] by tribocorrosion and electrochemical techniques. It was found that the effects of alloy and of albumin on corrosion depend on the base electrolyte: differences between LC and HC alloy were only observed in NaCl solutions but not in PBS. It was observed that albumin significantly increased corrosion of both alloys in PBS solutions while its effect in NaCl was smaller. It was concluded that the wear ranking of the HC and LC alloys also depends on the environment: HC Co-Cr-Mo alloy had lower wear resistance in NaCl and PBS + albumin than the LC alloy, while no differences between both alloys were found in the other solutions.

**Qiu J, Yu WQ, Zhang FQ, Smales RJ, Zhang YL and Lu CH (2011)<sup>47</sup>**

evaluated the corrosion behavior and surface properties of a commercial Co–Cr alloy and two Ni–Cr alloys [beryllium (Be) -free and -containing] before and after a simulated porcelain-firing process. In both as-cast and fired conditions, the Co–Cr alloy (Wirobond C) showed significantly more resistance to corrosion than the two Ni–Cr alloys. After firing, the corrosion rate of the Be-free Ni–Cr alloy (Stellite N9) increased significantly, which corresponds to a reduction in the levels of Cr, molybdenum (Mo), and Ni in the surface oxides and to a reduction in the thickness of the surface oxide film. The corrosion properties of the Co–Cr alloy and the Be-containing Ni–Cr alloy (Chang- Ping) were not significantly affected by the firing process. Porcelain firing also changed the microstructure and microhardness values of the alloys, and there was an increase in the release of Co and Ni ions, especially for Ni from the Be-free Ni–Cr alloy. It was concluded that the corrosion rate of the Be-free Ni–Cr alloy increased significantly after porcelain firing, whereas the firing

process had little effect on the corrosion susceptibility of the Co–Cr alloy and the Be-containing Ni–Cr alloy.

**Beck KA, Sarantopoulos DM, Kawashima I and Berzins DW (2012)**<sup>48</sup> compared the elemental release of new Co-Pd-Cr and Ni-Pd-Cr alloys with traditional Co-Cr and Ni-Cr alloys. Rectangular specimens from 5 different casting alloys with 6 samples in each were prepared and immersed in a lactic acid/ NaCl solution at 37°C for 7 days. Solutions were analyzed with ICP-AES to determine the elemental release. The concentrations of major ions (Co, Ni, Pd, Cr, and Mo) were compared using a generalized linear model ( $p < 0.05$ ). Representative specimens were examined with optical microscopy before and after immersion. It was found that Co-Pd-Cr alloys released a significantly greater amount of respective ions (Co, Cr, Mo, and total ions) compared to the traditional Co-Cr alloy. No significant differences in elemental release were noted between Ni-Pd-Cr and Ni-Cr. Optical microscopic examination showed abundant areas of corrosion in the palladium-containing Co-Cr alloys after immersion, whereas little difference was observed for the other alloys. It was concluded that corrosion resistance measured via elemental release was compromised when Co-Cr was alloyed with palladium, but this effect was not observed with Ni-Cr.

**Galo R, Ribeiro R, Rodrigues RC, Rocha LA and Mattos MG (2012)**<sup>49</sup> studied the effect of oral environment on the corrosion of dental alloys with different chemical composition using electrochemical methods (PDP and EIS). After corrosion testing, the Co-Cr dental alloy showed low current density and hence a high resistance to corrosion compared with the Ni-based dental alloys. The amount of Ni

ion (0.62 mg/L) and Cr ion (0.07 mg/L) released from Ni-Cr based (Ni-Cr and Ni-Cr-Ti) alloys was greater than the release of Co (0.01 mg/L) and Cr (0.03 mg/L) from Co-Cr based dental alloy. Some changes in microstructure were also observed that influenced the corrosion behavior of the alloys. It was concluded that the lower corrosion resistance led to a greater release of nickel ions to the medium. It was stated that the effect of artificial saliva on the corrosion of dental alloys and dissolution of the ions was strongly dependent on alloy composition.

**Al Subari R, Idrissi M, Draoui M, Bellaouchou A, Guenbour A and Merzouk N (2013)**<sup>50</sup> studied the effects of khat extract on the corrosion resistance of Ni-Cr dental alloys. The results showed that Kera N® and 4 all® alloys containing a high Cr and Mo content, shows the best corrosion resistance in artificial saliva compared with that of Commend® alloy. It was found that the corrosion resistance of three Ni-Cr alloys decreased by increasing the concentration of khat extract in artificial saliva. It was concluded that the presence of khat extract (*Catha edulis*) in artificial saliva accelerates the corrosion of Ni-Cr alloys and this could be due to the presence of fluoride, amino acids, tannic acid and ascorbic acid in khat.

**Andrysewicz E, Mystkowska J, Dąbrowski JR, Och E, Skolimowska K, Klekotka M (2013)**<sup>51</sup> evaluated the influence of human saliva and its six substitutes on the corrosion resistance of some implant alloys used in stomatology, which included: austenitic steel (316L), titanium alloy (Ti6Al4V), and cobalt alloy (Co-Cr-Mo). The results indicated an increased current density in the passive range on PDP curves of studied alloys in the environment of human saliva, and also in a commercial saliva solution (Mucinox). It can be concluded that in terms of corrosion resistance

the developed saliva substitutes can constitute competitive solutions to commercial saliva substitutes.

**Abey S, Mathew MT, Lee DJ, Knoernschild KL, Wimmer MA, Sukotjo C (2014)**<sup>52</sup> studied the electrochemical behavior and the influence of variable pH (3.0, 4.5, 6.0, 6.5, 7.5, and 9.0) on commercially pure titanium (CpTi) alloy in artificial saliva. The obtained PDP curves indicated behavior change at each pH. The corrosion current density value exhibited the poorest corrosion resistance for pH 7.5. The Nyquist plot (from the EIS results) showed the poorest resistance pH 7.5. SEM images indicated that pH levels of 6.5, 7.5, and 9.0 had considerable surface corrosion. It was concluded that the media's pH significantly influence the corrosion behavior of CpTi alloy in artificial saliva.

**Chen L, Zhang W and Zhang Y (2014)**<sup>53</sup> investigated the effect of chloride concentration on the corrosion of Co-Cr alloy and pure Ti in neutral artificial saliva solutions with different NaCl concentrations (0.9%, 2.0%, and 3.0%). The morphologies of corroded surface were observed by SEM analysis. The changes in  $E_{\text{corr}}$  for pure Ti and Co-Cr alloy in three kinds of artificial saliva solutions was not obvious. However, the self-corrosion current densities ( $I_{\text{corr}}$ ) of pure Ti were much lower than those of Co-Cr. The  $I_{\text{corr}}$  of Co-Cr alloy increased in a concentration-dependent manner of NaCl, whereas the breakdown potential ( $E_b$ ) of Co-Cr alloy decreased in a concentration-dependent manner. The potential ranged for the breakdown of an oxide film ( $E_v$ ) was shortened in a concentration-dependent manner of NaCl. There was no obvious difference in the  $I_{\text{corr}}$  of pure Ti with different concentrations of NaCl. The breakdown potential was not seen according to the

polarization curves. It was concluded that the increase of the concentration of Cl<sup>-</sup> accelerates the corrosion behavior of Co-Cr alloy, but it does not affect pure Ti.

**El Sawy AA and Shaarawy MA (2014)**<sup>54</sup> evaluated the amount of ions released from Ti6Al4V and Co-Cr-Mo alloys both *in vivo* and *in vitro*. The specimens from each group were immersed in a buffered saline solution over a period of 1, 3, 5, 7, 14, 21, and 28 days. It was concluded that the metallic ions released from the studied alloys were higher in the buffered saline solutions in the *in-vitro* than in the *in-vivo* study group and control group; however, these amounts were still within the physiological limit of trace elements in the human body.

**Puskar T, Jevremovic D, Williams RJ, Eggbeer D, Vukelic D and Budak I (2014)**<sup>55</sup> studied the corrosive effect of artificial saliva of variable pH (2.3, 4 and 6.8) on DMLS and cast Co-Cr-Mo dental alloy after an immersion period of 1, 7, 14 and 30 days. It was concluded that;

1. The metal elution in artificial saliva from the DMLS alloy was lower than the cast alloy.
2. Cobalt produced the greatest release of ions;
3. Acidity influenced the elution;
4. The greatest elution occurred in the most acidic environment, *i.e.*, 2.3 pH;
5. The longer the investigated period, the higher was the difference between the total metal ion release from the CM and DMLS alloys;
6. Both alloys (CM and DMLS) showed a safe level of elution according to the ISO definition in all investigated acidic environments.

**Qiao GY, Zhang LX, Wang J, Shen QP and Su JS.(2014)**<sup>56</sup> investigated the effect of epigallocatechin gallate (EGCG) on the surface properties of Ni-Cr dental alloys after electrochemical corrosion in 0 g/L and 1.0 g/L EGCG artificial saliva. The results showed serious corrosion on the surface of the alloy in 1.0 g/L EGCG artificial saliva than in 0 g/L EGCG. It was concluded that the corrosion resistance of Ni-Cr alloys becomes worse and the oxide content of corrosion products on the surface reduces in 1.0 g/L EGCG artificial saliva.

**Hedberg YS, Qian B, Shen Z, Virtanen S and Wallinder IO (2014)**<sup>57</sup> evaluated the influence of the non-equilibrium microstructure obtained by SLM, on corrosion susceptibility and extent of metal release. A multi-analytical approach was employed by combining microscopic and bulk compositional tools with electrochemical techniques and chemical analyses of metals in biologically relevant fluids for three differently SLM fabricated CoCrMo alloys and one cast CoCrMo alloy (used for comparison). It was found that Rapid cooling and strong temperature gradients during laser melting resulted in the formation of a fine cellular structure with cell boundaries enriched in Mo (Co depleted), and suppression of carbide precipitation and formation of a martensitic  $\epsilon$  (hcp) phase at the surface. These features were shown to decrease the corrosion and metal release susceptibility of the SLM alloys compared with the cast alloy. Unique textures formed in the pattern of the melting pools of the three different laser melted CoCrMo alloys predominantly explained observed significant, differences. It was concluded that the susceptibility to corrosion and metal release increased with an increased number (area) of laser melt pool boundaries.

**Xin X-Z, Chen J, Xiang N, Gong Y and Wei B (2014)**<sup>58</sup> examined the surface characteristics and corrosion properties of selective laser melted (SLM) cobalt–chromium (Co–Cr) dental alloys before and after porcelain-fused-to-metal (PFM) firing. It was found that the SLM specimens exhibited similar corrosion behavior before and after firing at both pH 5 and 2.5. Following firing, SLM samples displayed significantly better corrosion resistance than traditional cast specimens at pH 2.5. It was concluded that the corrosion properties of SLM Co–Cr specimens meet the needs of clinical applications and can exceed those of traditional cast specimens.

**Yang X, Xiang N and Wei B (2014)**<sup>16</sup> examined the effect of fluoride concentration on ion release from Co-Cr-Mo alloy specimens fabricated using selective laser melting and lost-wax casting in an artificial saliva solution containing NaF at concentrations of 0.00%, 0.05%, 0.1%, or 0.2%. The metal ion content of the solution was determined with an inductively coupled plasma mass spectrometer. It was found that the fluoride concentration significantly influenced the elemental ion release from both alloys. The quantity of ions released increased significantly with increasing fluoride concentration. The ion release from the cast specimens was significantly greater than that from the SLM specimens. It was concluded that the performance of the SLM alloy in immersion tests demonstrates that this new technique is a superior choice because of its good biocompatibility.

**Zeng L, Xiang N and Wei B (2014)**<sup>59</sup> compared the corrosion behavior of a Co-Cr-Mo alloy fabricated by the Selective Laser Melting (SLM) technique before and after ceramic firing, with that of traditional casting. It was concluded that the porcelain firing process had no significant influence on the corrosion resistance

results of the two alloys. Compared with traditional casting, selective laser melting alloy exhibited the same properties in both test solutions (pH 5.0 or 2.5).

**Alifui-Segbaya F, Lewis J, Eggbeer D and Williams RJ (2015)<sup>11</sup>** studied and compared the corrosion data obtained from additive manufactured heat-treated and non heat-treated Co-Cr alloy. The specimens were immersed in artificial saliva suspended by a nylon thread for 42 days at 37°C. Readings for Co, Cr and Mo ions released into solution were obtained using an atomic absorption spectrometer at 1, 4, 7, 14, 21, 28, 35, and 42 day intervals at a detection limit of one part per million (ppm). It was found that, after 42 days, the sum of Co-Cr-Mo released from heat-treated Co-Cr alloys was higher ( $1.65\pm 0.15\mu\text{g}/\text{cm}^2$ ) than non heat-treated Co-Cr alloys ( $0.06\pm 0.01\mu\text{g}/\text{cm}^2$ ). The study concluded that even though ion release in both samples was within the safe level recommended by ISO for the alloying elements, heat-treated laser sintered Co-Cr alloys contributed extensively to the reduced corrosion resistance.

**de Aguiar SR, Nicolai M, Almeida M and Gomes A (2015)<sup>60</sup>** studied the stability of the Co–Cr–Mo dental alloy immersed in artificial salivas (pH 6.7) over 24 h. Three artificial salivas were studied: saline saliva (saliva I); saline saliva buffered with phosphate ions (saliva II) and saliva II plus mucin molecules (saliva III). For all the systems, open circuit potential shift positively over 24 hours of immersion. Data extracted from the steady-state polarization curves demonstrated that the Co–Cr–Mo alloy had higher corrosion potential in saliva III, lower corrosion potential in saliva I and lower initial corrosion resistance in saliva III. After 24 hours of immersion in the artificial salivas, the Co–Cr–Mo alloy presents high corrosion stability, due to the

protective action created by the presence of corrosion products. From the analysis of the breakdown potential, it was concluded that, the presence of the phosphate ions and mucin promote the oxidation process, inducing the formation of etch pits. Regarding the effect of the mucin concentration in the corrosion behavior of the Co–Cr–Mo dental alloy, a negative shift was observed in the corrosion potential, pointing to a cathodic inhibitor role for the mucin molecules.

**Koutsoukis T, Zinelis S, Eliades G, Al-Wazzan K, Al Rifaiy M and Al Jabbari YS (2015)<sup>61</sup>** reviewed the effect of selective laser melting (SLM) procedure on the properties of dental structures made of Co-Cr alloys and evaluated its quality and compared it to those produced by conventional casting and milling fabrication techniques. It was concluded that the SLM technique provides dental prosthetic restorations more quickly and less expensively without compromising their quality compared with restorations prepared by casting and milling techniques.

**Lu Y, Wu S, Gan Y, Li J, Zhao C, Zhuo D, Lin J (2015)<sup>62</sup>** studied the microstructure, mechanical property and corrosion behavior of the selective laser melted (SLM) Ni-free Co-Cr-W alloy for the dental application. The line and island scanning strategy were applied to determine whether these strategies are able to obtain expected Co-Cr-W parts. The XRD analysis revealed that the  $\gamma$ -phase and  $\varepsilon$ -phase coexisted in the as-SLM Co-Cr-W alloys; The SEM images showed that the microstructure of Co-Cr-W alloys appeared square-like pattern with the fine cellular dendrites at the borders; tensile test suggested that the difference of mechanical properties of line- and island- formed specimens was very small; and the outcomes from the electrochemical and metal release tests indicated that the island-formed

alloys showed slightly better corrosion resistance than line-formed ones in PBS and Hanks solutions. Considering the mechanical properties and corrosion resistance of line-formed and island-formed specimens met the standards of ISO 22674:2006 and EN ISO 10271. It was concluded that Co-Cr-W dental alloys can be successfully fabricated by line and island scanning strategies in the SLM process.

**Lucchetti MC, Fratto G, Valeriani F, De Vittori E, Giampaoli S, Papetti P, Spica VR and Manzon L (2015)**<sup>14</sup> evaluated the ion release of Cr, Co, and Fe from the Co-Cr alloys used for traditionally cast and CAD-CAM dental devices after interaction with oral bacteria and different pH conditions. The specimens were prepared, polished, and immersed in 3 different pH media (artificial saliva [pH 2.3] and 6.5% and 0.9% saline solution [pH 7.1]). Specimens were also incubated in the presence of the bacterium *Eikenella corrodens*. Solutions were analyzed with an atomic absorption spectrometer after 15 and 30 days in the chemical corrosion test and 30 days in the biocorrosion test to detect ions released in different solutions. It was found that the greatest amount of element release was seen after 30 days: 4.964 ppm of casting alloy, 2.642 ppm of milling alloy, and 2.351 ppm of laser metal sintering. It was observed that Co-Cr alloys processed with different fabrication techniques show a release of low amounts of ions in all tested conditions. No difference was noted when the specimens were exposed to an enriched bacteria environment. It was concluded that all the alloys were adequately corrosion resistant and well suited for dental usage, although the casting alloy (LW) shows the greatest risk of corrosion under acidic conditions.

**Porcayo-Calderon J, Casales-Diaz M, Salinas-Bravo VM and Martinez-Gomez L (2015)<sup>15</sup>** investigated the Electrochemical properties (PDP, Cyclic polarization curves, measurements of OCP, and Linear polarization resistance) of austenite stainless steel used as biomaterials for dental use in two types of environments: artificial saliva and mouthwash solution at 37°C for 48 hours. The study compared these properties to titanium which is also a material commonly used in dental application. The results showed that tested steels have characteristics that make them attractive as biomaterials for dental applications. It was found that contents of Cr, Ni, and other minor alloying elements (Mo, Ti, and Nb) determine the performance of stainless steels. In artificial saliva, steels showed a corrosion rate of the same order of magnitude as titanium and in mouthwash have greater corrosion resistance than titanium. From PDP, it was concluded that in artificial saliva that stainless steels have corrosion rates higher than titanium and in mouthwash, this behavior was reversed.

**Puskar T, Lapcevic A, Arandjelovic S, Radulovic S, Budak I, Vukelic DJ and Jevremovic D (2015)<sup>63</sup>** investigated the cytotoxicity of direct metal laser sintered (DMLS) and cast Co-Cr-Mo (CCM) dental alloy. *In-vitro* tests were done on human fibroblast cell line MRC-5. The results showed that there was no statistically significant difference in the cytotoxic effects of DMLS and CCM alloy specimens. It was concluded that DMLS Co-Cr-Mo alloy have a good potential for application in dentistry.

**Siddharth R, Gautam R, Chand P, Agrawal KK, Singh RD and Singh BP (2015)<sup>64</sup>** evaluated the saliva of partially edentulous subjects rehabilitated with cast-

metal removable partial denture for leaching of different metals from denture. Saliva samples were taken at three stages that is, 1 h, 24 h and 72 h. It was found that at 1 h, 24 h and 72 h after the denture insertion, chromium (Cr) had statistically significant higher mean concentration as compared to manganese (Mn). Cr had maximum concentration (0.1479 + 0.0052) immediately after denture insertion while maximum concentration of Mn (0.1479 + 0.0052) was found 24 h after denture insertion. It was concluded that metal-based dentures show maximum leaching immediately after wearing of the prosthesis which decreased significantly over the period of 3 days. Cr and Mn were the metal ions mainly found in the saliva of cast partial denture wearer. No concentration of cobalt, molybdenum (Mo) and iron (Fe) was found in the saliva of metal base denture wearer. The results also showed a significant change in concentration of elutes in saliva in first 72 h/3 days making time an effective variable was observed.

**Sing SL, An J, Yeong WY and Wiria FE (2015)**<sup>65</sup> reviewed the current progress of two Additive manufacturing (AM) processes suitable for metallic orthopaedic implant applications, namely selective laser melting (SLM) and electron beam melting (EBM). The AM technology allows the direct fabrication of functional parts with complex shapes from digital models. The study stated the key advantage of this technology is that they do not have the design constraints that conventional manufacturing techniques have, allowing them to build complex geometries without a significant increase in building time. In addition, they require no tooling or moulds and enable the fabrications of several patient implants in the same batch, they are able to provide greater freedom of design to product developers and significantly lower the

customization cost. The study also focused on the SEM analysis and reviewed that the SLM part showed a compact homogeneous cellular microstructure with a much smaller grain size than cast part. This smaller grain size accounts for the better corrosion resistance in acidic conditions

**Tuna SH, Pekmez NÖ and Kürkçüoğlu I (2015)<sup>8</sup>** evaluated the electrochemical corrosion resistance of Co-Cr alloy specimens fabricated by conventional casting, milling, and laser sintering in artificial saliva. It was concluded that the corrosion resistance of a Co-Cr alloy specimens fabricated by milling or laser sintering was higher than that of the conventionally cast alloy specimens. The Co-Cr specimens manufactured by the same method also differed from one another in terms of corrosion resistance. These differences may be related to the variations in the alloy compositions.

**Băilă DI, Doicin CV, Cotruț CM, Ulmeanu ME, Ghionea IG and Tarb CI (2016)<sup>66</sup>** studied the FEM analysis and corrosion properties of two prototypes of dental elevator made by DMLS process, using a super alloy powder of Co-Cr (ST2724G), with Phenix Systems machine, type PXS & PXM Dental, one with a threaded tail and another with a cylindrical tail. The FEM analysis showed that the full metallic beak has the stress located ( $2,97 \times 10^8$  N/m<sup>2</sup>), smaller than the Co - Cr alloy material yield strength ( $1,2 \times 10^9$  N/m<sup>2</sup>). In vitro corrosion test in Fusayama Meyer artificial saliva ((pH 5.5 and at temperature  $37 \pm 1$  °C) presented an excellent corrosion resistance according to the different parameters that were measured:  $E_{oc}$ ,  $E_{corr}$ ,  $I_{corr}$ . It was concluded that both curved elevator prototypes can be used safely in surgical dentistry.

**Kim HR, Jang S-H, Kim YK, Son JS, Min BK, Kim KH and Kwon TY (2016)**<sup>67</sup> studied the microstructures and mechanical properties of cobalt-chromium (Co-Cr) alloys produced by three CAD/CAM-based processing techniques {milling (ML), selective laser melting (SLM), and milling/post-sintering (ML/PS)} and compared with those produced by the traditional casting (CS) technique. It was found that the SLM group showed superior mechanical properties, the ML/PS groups were nearly comparable to each other. The mechanical properties of the ML group were inferior to those of the CS group. It was concluded that the microstructure of the alloys was strongly influenced by the manufacturing processes as well as the chemical composition. The SLM and ML/PS techniques may be considered promising alternatives to the Co-Cr alloy casting process.

**Qian C, Wu X, Zhang F and Yu W (2016)**<sup>68</sup> evaluated the surface properties and corrosion behaviors of Ni-free Co-Cr-Mo and Co-Cr-Mo-Ni dental casting alloy for partial removable dental prosthesis frameworks in artificial saliva at pH values of 5.0 and 2.5. It was found that the relative levels of Co and Cr of the surface composition were higher in the Co-Cr-Mo alloy. The Co-Cr-Mo alloy had statistically higher surface hardness than the Co-Cr-Mo-Ni alloy. In the pH 2.5 environment, both of the alloys showed a decreased corrosion resistance. The microstructure of the Co-Cr-Mo-Ni alloy corroded more than that of the Co-Cr-Mo alloy in the pH 2.5 environment. The oxide-layer corrosion resistance of the Co-Cr-Mo alloy was better than that of the Co-Cr-Mo-Ni alloy in Fusayama artificial saliva solutions at pH values of both 5.0 and 2.5. It was concluded that the corrosion resistance of the Co-Cr-Mo alloy was better in the oral environment, especially at a low pH value.

**Alageel O, Abdallah MN, Alsheghri A, Song J, Caron E and Tamimi F (2017)**<sup>69</sup> characterized the mechanical, physical, and biocompatibility properties of cobalt–chromium (Co–Cr) alloys produced by two laser-sintering systems {Selective Laser-Sintering method using the Phenix system (L-1) and the Direct Metal Laser-Sintering method using EOS system (L-2)} and compared them to those prepared using conventional casting methods (CC). It was found that Co–Cr alloys processed by L-1 and L-2 techniques were 8 and 3.5 times more precise than the CC technique. The L-1 and L-2 techniques showed higher hardness, yield strength, and fatigue resistance compared to CC alloys. In terms of biocompatibility, both techniques were equally biocompatible. It was concluded that laser-sintered RPD's could present clinical benefits over cast ones.

**Lucia D (2017)**<sup>70</sup> evaluated and compared the investment casting and DMLS technique focusing on dental applications for prosthesis production. It was found that DMLS of Co-Cr produces prosthesis of excellent strength and without any defects. It was concluded that DMLS is very reliable and repeatable technique. The SEM analysis showed that the particles were strongly joined together; not only with each layer but also between different layers and the isotropy in build direction is a rarity. From a mechanical point of view, it was concluded that the DMLS technique has higher performance with respect to the investment casting.

**Mercieca S, Caligari Conti M, Buhagiar J and Camilleri J (2017)**<sup>71</sup> studied and compared the degradation resistance of Ni-Cr and Co-Cr alloys used as a base material for partial dentures in contact with saliva. It was found that the Co-Cr alloy was more stable and showed superior corrosion performance than the Ni-Cr alloy in

all solutions tested. It was concluded that Ni-Cr alloys are unstable in solution and leach nickel. Therefore, Co-Cr alloys should be preferred for clinical use.

**Lu C, Zheng Y and Zhong Q (2017)**<sup>72</sup> studied the corrosion properties of CoCr and NiCr alloys in artificial saliva (AS) containing tryptic soy broth (Solution 1) and *Streptococcus mutans* (*S.mutans*) species (Solution 2) by electrochemical methods, including OCP, EIS and PDP. The adherence of *S. mutans* to the alloy surfaces immersed in Solution 2 for 24 h was verified by SEM. The obtained EIS results confirmed that the biofilm formation played an important role in the alloy corrosion process, while the presence of *S. mutans* in the solution reduced the corrosion rate of the studied alloys. A negative shift of the OCP with immersion time was observed for all samples regardless of the solution type. It was concluded that the biofilm formation observed after 24 h of exposure to *S. mutans* bacteria might enhance the corrosion resistance of the studied samples by creating physical barriers that prevented oxygen interactions with the metal surfaces.

# *Materials and method*

*Methodology should not be a fixed tract to a fixed destination but a conversation about everything that could be made of happen*

This study was carried out to evaluate and compare the corrosion rate of conventional and Direct Metal Laser Sintered (DMLS) Co-Cr dental alloys in fluoride solution.

The description of this study is divided into following subheadings:

1. Materials
2. Armamentarium
3. Equipments
4. Method

## 1. MATERIALS: (Plate 1)

The materials used were as follows:

### Co-Cr alloys: - (Plate I, Fig.1 and 2)

SR.NO	ALLOY	COMPOSITION (WEIGHT %)	COMPONENT CHARACTERISTICS	BATCH NO.
1.	Bego wironit® Co-Cr alloy (REF: 50030)	Co: 64% Cr: 28.6% Mo: 5% Si Mn C	ISO standard (22674):-Type 5 Density:- 8.2 g/cm <sup>3</sup> Melting range:- 1320–1350°C Casting temperature:-1450°C Ductile yield(A <sub>5</sub> ):- 6.2% Tensile strength (R <sub>m</sub> ):- 800MPa Elongation limit (R <sub>p0.2</sub> ):- 600MPa Modulus of elasticity:-approx. 211 GPa Vickers hardness (HV10):- 350 HV (from product manual)	12635
2.	EOS- SP2Co- Cr alloy powder (REF: 9011- 0018)	Co: 63.8% Cr: 24.7% Mo: 5.1% W: 5.4% Si: 1.0% Fe: max. 0.5% Mn: max. 0.1% (free of Ni, Be and Cd)	ISO standard (22674):- Type 4 Density:- 8.5 g/cm <sup>3</sup> Proof Strength(R <sub>p0.2</sub> %):- 850 Ultimate Tensile strength:- 1350 Mpa Percentage elongation:- 3% Young's Modulus:- approx. 200 Gpa Vickers hardness (HV10):- 420 HV Coefficient of Thermal expansions :(25-500°C):- 14.3 x 10E- 6.m/m°C :(20-600°C):- 14.5 x 10E- 6.m/m°C Melting interval:- 1410°C - 1450 °C (from product manual)	H291201

**Materials used for casting and laser Sintering of Co-Cr alloys: - (Plate I, Fig.3, 4 and 5)**

<b>SR. NO.</b>	<b>TYPE OF SOLUTION</b>	<b>TRADE NAME</b>	<b>MANUFACTURER</b>	<b>BATCH NO.</b>
1.	Pattern RM Resin	GC	GC India Dental Pvt Ltd.	1504221
2.	Sprue wax (4mm)	Maarc	Maarc	--
3.	Investment material	Wirovest®	Bego	0207421
4.	Mixing liquid	BegoSol®	Bego	REF-51090
5.	Debubblizer	PDP debubblizer	Prime Dental products	16102-02

**Powders used for making solutions: -(Plate I, Fig.6)**

<b>SR. NO.</b>	<b>TYPE OF SOLUTION (Per 1000 ml.)</b>	<b>MANUFACTURER</b>	<b>BATCH NO.</b>
1.	NaCl	Fisher's Scientific	2844990116
2.	KCl	Fisher's Scientific	2844680116
3.	CaCl <sub>2</sub> . 2H <sub>2</sub> O	S.d.fine-chem Ltd.	AOOZ-0119-2310-13
4.	NaH <sub>2</sub> PO <sub>4</sub> . 2H <sub>2</sub> O	Lobachemie	LB242009
5.	Na <sub>2</sub> S. 9H <sub>2</sub> O	Merck	106657
6.	Urea	Lobachemie	46016
7.	Double distilled water	--	--
8.	NaF 0.2%	S.d.fine-chem Ltd.	S/1193/993/281011

**Materials used for mounting and polishing of the samples: - (Plate I, Fig.7 and 8)**

<b>SR. NO.</b>	<b>MATERIAL</b>	<b>TRADE NAME</b>	<b>MANUFACTURER</b>	<b>BATCH NO.</b>
1.	Silver conducting paste	Silver conducting adhesive	Coatex industries	--
2.	Self-cure PMMA acrylic resin	DPI- RR cold cure	DPI	10162
3.	Alumina polishing powder	Extec® alumina powder	Extec	--

**2. ARMAMENTARIUM: (Plate II)**

**Armamentarium for Cast and DMLS samples: - (Plate II, Fig. 9 and 10)**

1. Master model made of brass alloy
2. Casting Ring
3. Casting Ring liner
4. Sprue wax (4mm) and vent wax
5. Abrasive disks (coarse)
6. Rubber mixing bowl and spatula
7. Abrasive rubber wheels and carbide burs

**Armamentarium for making solutions, mounting & polishing of samples: - (Plate II, Fig.11 and 12)**

1. Copper wire
2. Copper tube
3. Solder wire

4. Emery papers (200- 1500#)
5. Polishing cloth
6. Alumina powder (75  $\mu\text{m}$ )
7. Embedding mold

**Miscellaneous armamentarium: - (Plate II)**

1. Digital vernier Caliper (+/- 0.01mm)
2. Plaster spatula
3. Separating medium
4. Dappen dish
5. Glass slab
6. Scissors
7. Cutter
8. Petroleum jelly
9. Carver
10. Wax knife & Wax spatula
11. Cutter
12. Silicone jar
13. Beaker and stirrer

**3. EQUIPMENTS: (Plate III, Fig. 13-20)**

<b>SR.NO.</b>	<b>EQUIPMENT</b>	<b>MANUFACTURER</b>
1.	Vacuum Mixer	Sirio
2.	Burnout furnace	Sirio
3.	Induction Casting Machine	Ducatron

4.	Sand blaster	Minisab 2 T
5.	EOSINT M270 DMLS machine	e-manufacturing solutions
6.	Micromotor and Handpiece	D.R.S. Marathon
7.	Weighing machine	Tovatech
8.	Double distilled water equipment	Biobase
9.	Digital pH meter	Systronics
10.	Grinder polisher machine ( <b>Plate V</b> )	Chennai Metco Bain pol
11.	Oven	Sonar industries
12.	Ultrasonicator	Bio-technics India™
13.	Thermostat ( <b>Plate V</b> )	Cyberlab CB
14.	Potentiostat	BioLogic

#### **4. METHOD: (Plate IV, V & VI)**

The methodology was as follows:

- A. Preparation of samples
  - i. Fabrication of Cast samples
  - ii. Fabrication of DMLS samples
- B. Mounting and surface preparation of Samples
- C. Preparation of test solution/ corrosive electrolytes
- D. Electrochemical corrosion testing

#### **A. PREPARATION OF SAMPLES: -**

A total of 40 samples (20 samples from cast and other 20 samples for DMLS) were prepared.

Test condition (40)	Control group- AS (20)		Experimental group- ASF (20)	
	Cast subgroup C (10)	DMLS subgroup D (10)	Cast subgroup C (10)	DMLS subgroup D (10)
Non stored - N	Div CN	Div DN	Div CNF	Div DNF
Stored -S	Div CS	Div DS	Div CSF	Div DSF

\* Artificial saliva: - AS, Artificial saliva containing fluoride: - ASF and Fluoride: - F

\* Subgroups: - Cast (C), DMLS (D) and Test conditions: - Non-stored (N), Stored(S)

The samples of Control groups were tested in AS test electrolyte, while the samples of the Experimental groups were tested in ASF test electrolyte.

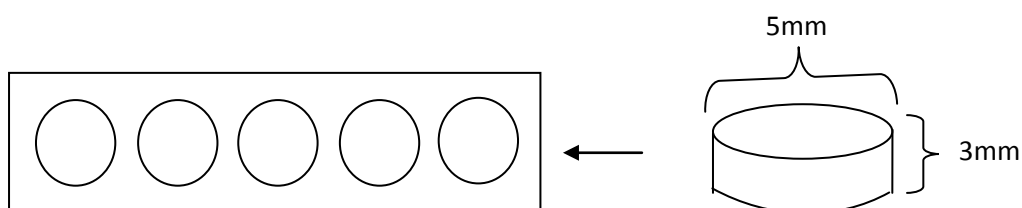
**i) Fabrication of cast samples:**

The steps were:-

1. Metal mold fabrication
2. Casting procedure

**1. Metal mold fabrication:**

A rectangular Brass metal mould containing 5 disc-shaped holes of diameter 5mm and thickness 3mm was designed.(Plate IV, fig. 21)The mold was provided with a 2 mm of screw head at the bottom for easy removal of the sample.



This mold was used for obtaining pattern resin samples, each of same dimensions. The patterns were then sprued with a 4mm diameter sprue wax.

## **2. Casting procedure:**

Four patterns per ring were invested (**Plate IV, Fig. 22**) in graphite-free, phosphate-bonded investment material with a powder- liquid ratio of 100 grams of powder to 15 ml. of liquid (as per product manual).The invested mould was allowed to set for 30 minutes and then was heated gradually at 250°C (insertion temperature and holding level) and 900°C (final temperature) for 60 minutes in a burnout furnace. Casting was performed in an induction casting machine as per manufacturer's instructions. Cast moulds were allowed to bench-cool for an hour before they were divested. The samples were sandblasted with 50 µm aluminum oxide powder. Sprues were subsequently separated from samples using coarse abrasive disk. A micro-motor hand-piece fitted with carbide burs was used to remove casting beads on the test samples. Total 20 samples were fabricated for further processing. (**Plate IV, Fig. 25**)

### **ii) Fabrication of DMLS samples:**

A cylinder of 5mm x 3mm dimension was created in Netfabb software (3D CAD) and a **STL** file of the same dimension was obtained (**Plate IV, Fig.23**), which was then put in Cambridge software for the slice file i.e. in **'SLI'** file format which is accepted by DMLS machine. This slice file was then sent to the DMLS machine's computer program **'RP tools'**. At this stage, the geometry of 3D model was properly oriented for part building. Once this "build file" was completed, it instructs the DMLS machine to begin the build-up process. Inside the build chamber area, there is a material dispensing platform (250mm x 250mm) and a build platform along with a

recoater blade used to move new powder over the build platform. It fuses metal powder into a solid part by sintering it locally using the focused laser beam (200 watt Yb-fiber optic laser) (**Plate IV, Fig. 24**). Parts were built up additively layer by layer, typically using layers of 20  $\mu\text{m}$  thickness. This sintering continued until final dimension of the samples was obtained. The surfaces of samples were prepared using carbide burs. All samples were subsequently polished on one flat surface with abrasive rubber wheels. Total 20 samples were obtained. (**Plate IV, Fig. 26**)

Processing parameters used for sample fabrication on the EOSINT M270 were as follows: - (from product manual)

<b>Processing parameter</b>	<b>Part border</b>	<b>Part hatch (core)</b>
Laser power (W)	200	200
Laser point distance ( $\mu\text{m}$ )	70	85
Laser exposure time (ns)	50	80
Laser beam spot compensation (mm)	0.079	0.079

**B. MOUNTING AND SURFACE PREPARATION OF CAST AND DMLS SAMPLES: -**

Initially, the copper strip was soldered to the electrical wire. This copper strip was then attached to the individual sample using silver paste, to provide the conductivity from the electrical wire to the sample. (**Plate V, Fig.27**) After this, all the sides of the samples were embedded with a self cure acrylic resin to expose only one side of the sample, wherein the surface area of the exposed side was  $0.196 \text{ cm}^2$ .

All the mounted samples were then mirror polished for the corrosion investigation. **(Plate V, Fig.28)** Firstly, the samples were abraded with series of emery paper (#150, 400, 600, 800, 1200 and 1500). Secondly, cloth polishing smeared with alumina was performed to get the perfect mirror polishing using a grinder-polisher machine. After mirror polishing, samples were ultrasonically cleaned in ethanol for 15 minutes **(Plate V, Fig.29)** and washed in distilled water to remove the surface contaminants.<sup>8, 25</sup>

### **C. PREPARATION OF TEST SOLUTION/ CORROSIVE ELECTROLYTES: -**

The corrosion behavior of control group was evaluated in artificial saliva solution (AS), while experimental group was evaluated in artificial saliva solution containing 0.2 % NaF (ASF).

The AS solution was freshly prepared before each experiment and was composed of 0.400 gm. NaCl; 0.400 gm. KCl; 0.906 gm. CaCl<sub>2</sub>, 2H<sub>2</sub>O; 0.690 gm. NaH<sub>2</sub>PO<sub>4</sub>, 2H<sub>2</sub>O; 0.005 gm. Na<sub>2</sub>S, 9H<sub>2</sub>O; and 1.000 gm. urea and diluted with double distilled water to 1000 ml. Test conditions were: pH 5.3 (maintained at this pH, by buffering with lactic acid) and 37±1°C temperature, to simulate the clinical situations.<sup>8</sup>

The ASF solution was prepared with NaF, at a concentration of 0.2% (2 gm. of NaF in 1000 ml. of artificial saliva solution).<sup>16, 25</sup>

Samples of stored groups were immersed in respective solutions at 37±1°C and pH 5.3 in an oven for 2 months. **(Plate V, Fig.30)**

#### D. ELECTROCHEMICAL CORROSION TESTING: -

A potentiostat connected to a computer was used to carry out electrochemical measurements at  $37\pm 1^\circ\text{C}$  (chiller was used to maintain the temperature) in a 300 ml. of artificial saliva solution, buffered with lactic acid to a pH of 5.3 (open to atmosphere). Electrochemical measurements were performed in a 3-electrode cell<sup>8, 40</sup> setup consisting of sample as working electrode, platinum foil as the counter electrode and saturated calomel electrode as reference electrode (**Plate V, Fig.31 & 32**). Before corrosion tests and surface examination, the electrodes were mechanically ground with several metallographic abrasive papers (#s180-, 400-, 600-, 1000-, 1200-grit). Then after being ultrasonically cleaned in acetone for 3 min they were polished with 3  $\mu\text{m}$  grit diamond paste degreased in acetone and rinsed with distilled water.<sup>6</sup> In electrochemical measurement, a potential was applied between the reference and working electrode, and the resulting current transmitted between the working electrode and the counter electrode was recorded. Before the Potentiodynamic Polarization (PDP) test, the alloy was cleaned potentiostatically for 10 minutes, at a potential of -1.2 V, to eliminate the effects of any surface oxides and impurities. Potentiodynamic polarization tests were conducted from -0.5 V (vs. OCP) up to +1.6 V (vs. OCP) at a scan rate of  $0.2\text{ mV s}^{-1}$  (as per ASTM standard). Minimum of at least 3 experiments were performed to ensure the reproducibility of the results.<sup>8, 25</sup>

The obtained potentiodynamic polarization (PDP) curves (**Annexure**) were analyzed using the curve-fitting routine of the specialized EC Lab software to calculate the electrochemical data (corrosion potential-  $E_{\text{corr}}$  value and corrosion current density-  $I_{\text{corr}}$  value)<sup>25</sup> using Tafel extrapolation method. These values were then preceded for statistical analysis.

The post corrosion test samples are mentioned in **Plate VI**.

# PLATE I (MATERIALS)



Fig.1. Bego wironit® Co-Cr alloy



Fig.2. EOS-SP2 Co-Cr alloy powder



Fig.3. Investment material and Mixing liquid



Fig.4. Pattern resin.



Fig.5. Debubblizer



Fig.6. All chemicals



Fig.7. Silver paste



Fig.8. Self cure PMMA resin

## PLATE II (ARMAMENTARIUM)



**Fig.9. Materials for fabrication of patterns**



**Fig.10. Materials for Casting**



**Fig.11. Materials for making solutions**



**Fig.12. Materials for mounting and polishing**

## PLATE III (EQUIPMENTS)



**Fig.13. Burnout furnace**



**Fig.14. Induction Casting machine**



**Fig.15. Sandblaster**



**Fig.16. pH meter**



**Fig.17. Soldering machine**



**Fig.18. EOS M270 DMLS machine**



**Fig.19. Double distilled water equipment**



**Fig.20. Potentiostat (BioLogic)**

## PLATE IV (METHODOLOGY)

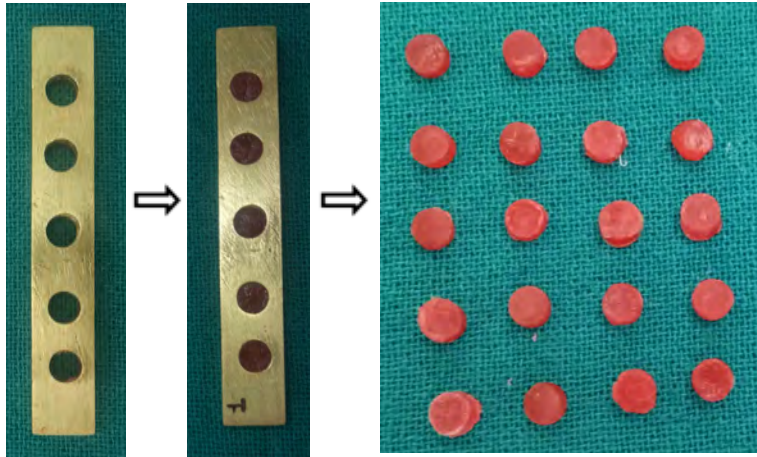


Fig.21. Brass metal mould used for obtaining pattern resin samples for Casting

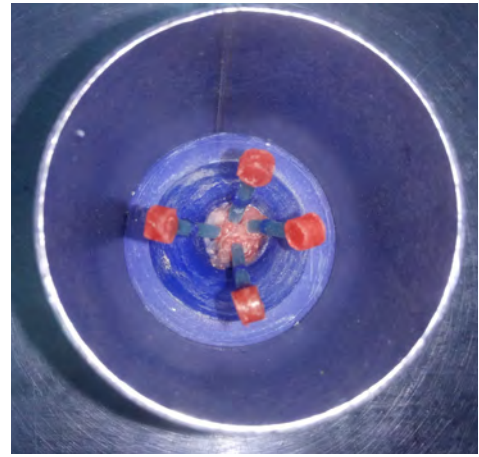


Fig.22. Patterns sprued and ready for investing

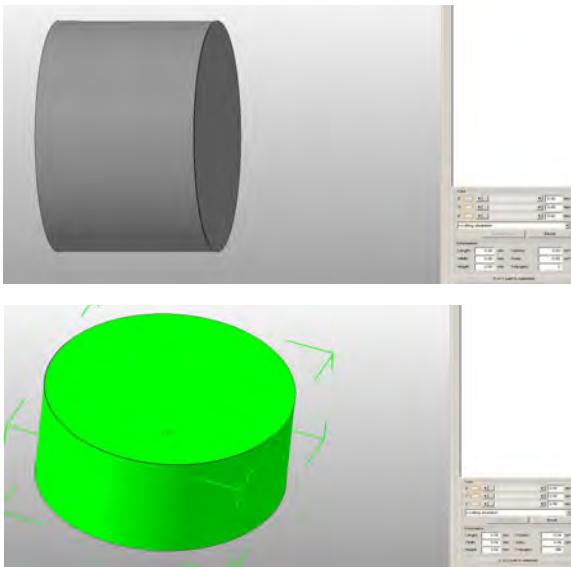


Fig.23. STL file

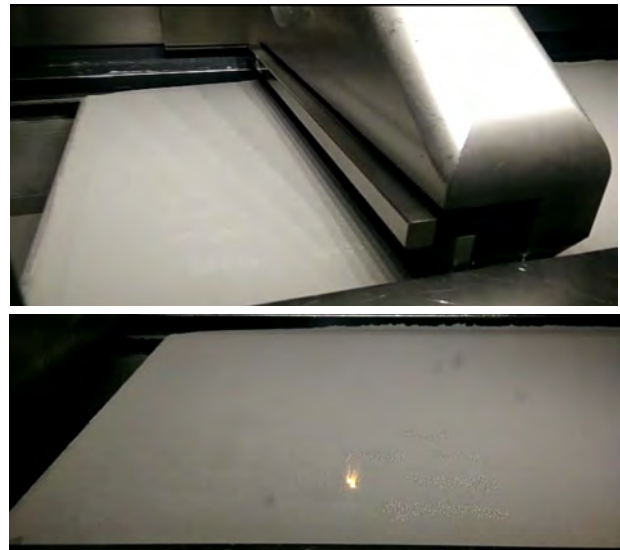


Fig.24. Laser sintering at platform

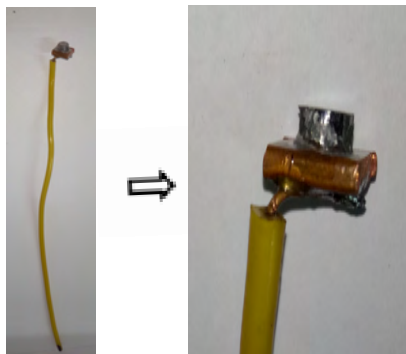


Fig.25. Cast samples (20)

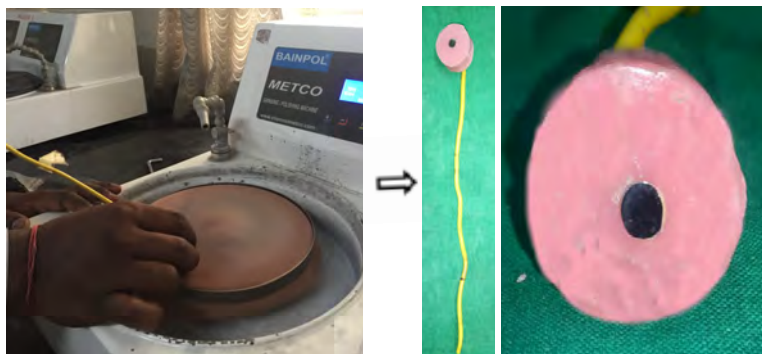


Fig.26. DMLS samples (20)

## PLATE V (METHODOLOGY)



**Fig.27. Soldering and attaching the sample to the copper wire with Silver conducting paste**



**Fig.28. Mirror finishing of mounted samples at grinder polisher machine**



**Fig.29. Samples kept in Ultrasonic Bath**



**Fig.30. Storage of samples in an Oven**



**Fig.31. Three electrode EC cell set-up**

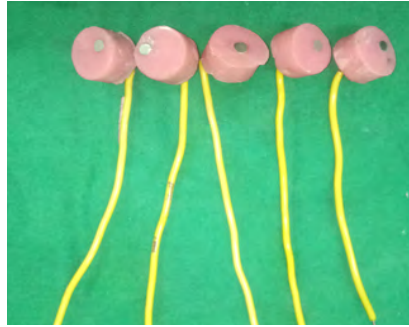


**Fig.32. EC cell set-up attached to the wires of potentiostat in chiller (Thermostat) maintained at  $37\pm 1^\circ\text{C}$**

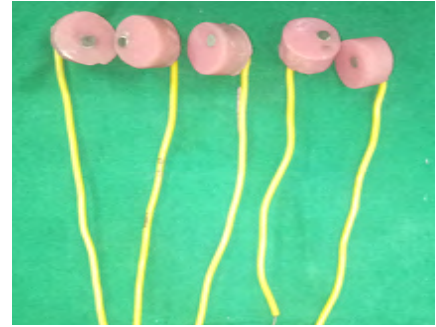


**Fig.33. Corroded sample after testing**

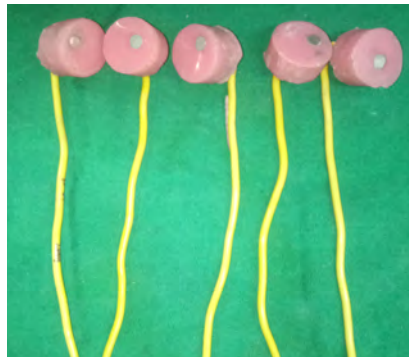
## PLATE VI (POST-TEST SAMPLES)



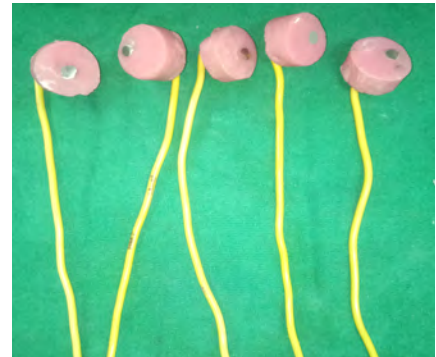
34.a) Div. CN



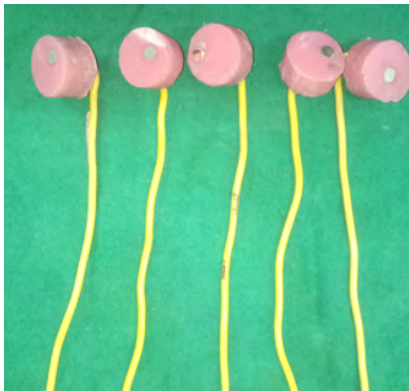
34.b) Div. DN



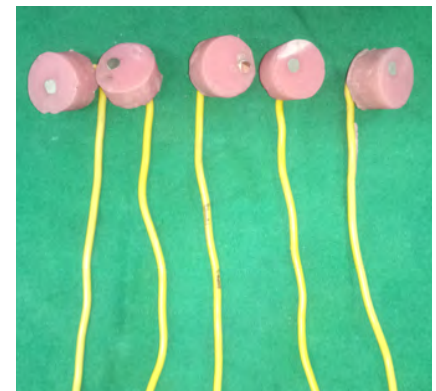
34.c) Div. CNF



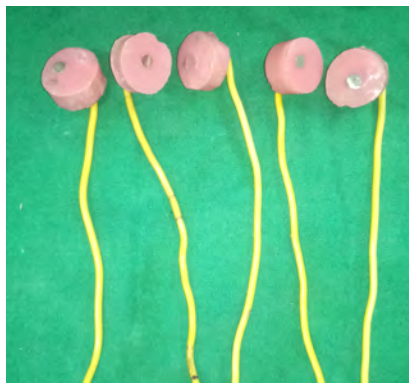
34.d) Div. DNF



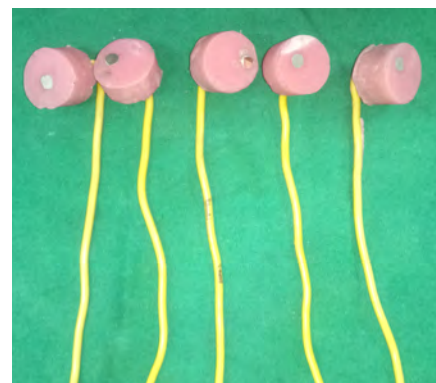
35.a) Div. CS



35.b) Div. DS



35.c) Div. CSF



35.d) Div. DSF

Fig.34. Test condition N

Fig.35. Test condition S

## Results

*Life is like a mirror, we get the best results when we smile*

In this study, the corrosion behavior of Co-Cr alloy was evaluated using two different fabrication methods i.e. conventional casting using lost wax technique and DMLS procedure, in fluoride solution.

Out of 40 samples, 20 samples were subjected to corrosion testing without any storage while the other 20 samples were stored for 2 months in the corrosive test electrolytes and preceded for electrochemical corrosion testing. Test and storage conditions of the corrosive test solutions were at pH 5.3 and temperature  $37\pm 1^\circ\text{C}$ .

The corrosion testing was done using Potentiostat attached to the computer. The PDP plots (Annexure) obtained for the samples showed the current-potential relationship. The sample potential was scanned in the positive direction and therefore

acted as anode such that it corrodes or forms an oxide coating. These plots were then used to determine the  $E_{\text{corr}}$  (corrosion potential) and  $I_{\text{corr}}$  (corrosion current density) values by Tafel extrapolation method. (Annexure- PDP plots and Master chart)

The sample grouping was done as follows:-

Test condition (40)	Control group –AS (20)		Experimental group- ASF (20)	
	Cast Subgroup C (10)	DMLS Subgroup D (10)	Cast Subgroup C (10)	DMLS Subgroup D (10)
Non stored - N	Div CN	Div DN	Div CNF	Div DNF
Stored -S	Div CS	Div DS	Div CSF	Div DSF

#### STATISTICAL ANALYSIS:-

Data from the cast and DMLS samples regarding the electrochemical corrosion testing in AS and ASF solutions were obtained and summarized in terms of mean and standard deviation. The tests were performed at two instances i.e. N and S test conditions.

Two-way analysis of variance was performed independently at two different test conditions i.e. N and S. Two factors were considered viz.

1. **Between groups:-** Presence or absence of fluoride in the test solution; Control (Group AS) and Experimental (Groups ASF)
2. **Between subgroups:-** Manufacturing method ; casting (Subgroup C) and DMLS (Subgroup D)

All the analyses were performed using SPSS ver 20.0 (IBM Corp.) software and the statistical significance was tested at 5% level.

The methods used are detailed as below:

### **Two-way analysis of variance**

Let there be two factors A and B at  $a$  and  $b$  levels respectively. Let  $x$  denote the variable under study, such that  $x_{ijk}$  ( $i=1, 2, \dots, a; j=1, 2, \dots, b, k=1, 2, \dots, r$ ) represent the  $k^{\text{th}}$  observation from  $i^{\text{th}}$  level of factor A and  $j^{\text{th}}$  level of factor B.

The two-way ANOVA will test for the main effects of factor A or B, namely,

$H_0: \mu_1 = \mu_2 \dots = \mu_a$  for factor A and

$H_1: \mu_{.1} = \mu_{.2} \dots = \mu_{.b}$  for factor B

Finally, each observation  $x_{ijk}$  can be expressed as  $x_{ijk} = \mu + a_i + b_j + c_{ij} + e_{ijk}$  where  $e_{ijk}$  denotes the error (unexplained component).

The two factors A and B are said to fixed factors and the model is the fixed effects model. For such model with equal number of observations per cell, the total sum of squares is given by the expression:

$$SS(\text{total}) = SS(A) + SS(B) + SS(AB) + SSE$$

Where AB is the interaction effect due to factors A and B.

Various formulae for estimating these sum of squares are as below:

The total sum of squares is given by

$$SS(total) = \sum_i \sum_j \sum_k (x_{ijk} - \bar{x}...) ^2 \text{ with } n-1 \text{ degrees of freedom.}$$

Sum of squares due to factor A is given by

$$SSA = rb \sum_i (\bar{x}_{i..} - \bar{x}...) ^2 \text{ with } a-1 \text{ degrees of freedom.}$$

Similarly, sum of squares due to factor B is given by

$$SSB = ra \sum_j (\bar{x}_{.j.} - \bar{x}...) ^2 \text{ with } b-1 \text{ degrees of freedom.}$$

Sum of squares due to interaction is given by

$$SS(AB) = r \sum_i \sum_j (x_{ij.} - \bar{x}_{i..} - \bar{x}_{.j.} + \bar{x}...) ^2 \text{ with } (a-1)(b-1) \text{ degrees of freedom}$$

And sum of squares due errors is given by

$$SSE = \sum_i \sum_j \sum_k (x_{ijk} - \bar{x}_{ij.}) ^2 \text{ with } (n-ab) \text{ degrees of freedom}$$

Accordingly, the mean sum of squares are:

$$MST=SS(total)/(n-1); MSA=SSA/(a-1); MSB=SSB/(b-1); MS(AB)=SS(AB)/(a-1)(b-1)$$

$$MSE=SSE/(n-ab)$$

The  $F$ -statistic for each factor could be obtained as:

$$F_{(a-1, (n-ab))} = MSA/MSE \text{ for factor A,}$$

$$F_{(b-1, (n-ab))} = MSB/MSE \text{ for factor B and interaction effect}$$

$$F_{((a-1)(b-1), (n-ab))} = MS(AB)/MSE$$

Thus, the decision of accepting or rejecting the null hypothesis can be taken from  $F$ -statistic.

---

The statistical analysis was done in two parts:-

1. For Corrosion potential ( $E_{\text{corr}}$ )
2. For Corrosion current density ( $I_{\text{corr}}$ )

### 1. STATISTICAL ANALYSIS FOR $E_{\text{corr}}$ :-

**Table 1** provides the descriptive statistics of  $E_{\text{corr}}$  for groups AS and ASF; and subgroups C and D at test conditions N and S.

For test condition N: -In the AS group, the mean  $E_{\text{corr}}$  value for Div CN was  $-179.23 \pm 2.66$  mV and for Div DN was  $-151.37 \pm 0.78$  mV. In the ASF group, the mean  $E_{\text{corr}}$  value for Div CNF was  $-259.37 \pm 2.74$  mV and for Div DNF i.e.  $-236.47 \pm 1.49$  mV.

For test condition S: -In the AS group, the mean  $E_{\text{corr}}$  value for Div CS was  $-23.35 \pm 1.33$  mV and for Div DS was  $-8.22 \pm 3.47$  mV. In the ASF group, the mean value for Div CSF was  $-37.06 \pm 1.99$  mV and for Div DSF was  $-18.04 \pm 2.51$  mV.

Comparison of  $E_{\text{corr}}$  values 'between Div's' of each subgroup between test conditions N and S revealed statistically highly significant difference as indicated by P-values  $< 0.0001$  using paired t-test, as shown in **Table 1**.

Two-way Analysis of variance was performed for  $E_{\text{corr}}$  values at test conditions N and S, as shown in **Table 2 and 3** respectively.

At test condition N, the 'between groups' effect was statistically highly significant with P-value  $< 0.0001$ . Also, the 'between subgroups' effect was statistically highly significant with P-value  $< 0.0001$ , as shown in **Table 2**.

On similar lines, at test condition S, the ‘between groups’ effect was statistically highly significant with P-value < 0.0001 and the ‘between subgroups’ effect was also statistically highly significant with P-value < 0.0001, as shown in **Table 3**.

**Column chart 1** shows the representation of mean corrosion potential ( $E_{\text{corr}}$ ) between groups and subgroups at test conditions N and S. The highest mean  $E_{\text{corr}}$  value obtained was for Div DS, followed by Div’s DSF, CS, CSF, DN, CN, DNF, CNF.

## 2. STATISTICAL ANALYSIS FOR $I_{\text{corr}}$ :-

**Table 4** provides the descriptive statistics of  $I_{\text{corr}}$  for groups AS and ASF; and subgroups C and D at test conditions N and S.

For test condition N: - In the AS group, the mean  $I_{\text{corr}}$  value for Div CN was  $0.15 \pm 0.02 \mu\text{A}/\text{cm}^2$  and for Div DN was  $0.06 \pm 0.02 \mu\text{A}/\text{cm}^2$ . In the ASF group, the mean value for Div CNF was  $0.21 \pm 0.07 \mu\text{A}/\text{cm}^2$  and for Div DNF  $0.17 \pm 0.11 \mu\text{A}/\text{cm}^2$ .

For test condition S: - In the AS group, the mean  $I_{\text{corr}}$  value for Div CS was  $0.02 \pm 0.01 \mu\text{A}/\text{cm}^2$  and for Div DS was  $0.01 \pm 0.01 \mu\text{A}/\text{cm}^2$ . In the ASF group, the mean value for Div CSF was  $0.07 \pm 0.03 \mu\text{A}/\text{cm}^2$  and for Div DSF was  $0.02 \pm 0.01 \mu\text{A}/\text{cm}^2$ .

Comparison of  $I_{\text{corr}}$  values ‘between Div’s’ of each subgroup at test conditions N and S revealed statistically significant difference as indicated by P-values < 0.05 using paired t-test, as shown in **Table 4**.

Two-way analysis of variance was performed for the  $I_{\text{corr}}$  values at test conditions N and S, as shown in **Table 5 and 6** respectively.

At the test condition N, the ‘between groups’ effect was statistically significant with P-value of 0.005. Also, the ‘between subgroups’ effect was statistically significant with P-value of 0.046, as shown in **Table 5**.

At test condition S, the ‘between groups’ effect was statistically significant with P-value of 0.006. Also, the ‘between subgroups’ was statistically significant with P-value of 0.002, as shown in **Table 6**.

**Column chart 2** shows the representation of mean corrosion current density ( $I_{\text{corr}}$ ) between groups and subgroups at test conditions N and S. The highest mean  $I_{\text{corr}}$  value obtained was for Div CNF, followed by Div’s DNF, CN, CSF, DN, CS and DSF, DS.

# *Discussion*

## *Discussion is an exchange of knowledge*

In this changing economic environment, humans are more fastidious than ever. Oral health is essential to the general health and well-being of individuals and the population.<sup>73</sup> Prosthodontics is the dental specialty pertaining to the diagnosis, treatment planning, rehabilitation, and maintenance of the oral function, comfort, appearance, and health of patients with clinical conditions associated with missing or deficient teeth and/or maxillofacial tissues using a biocompatible substitute, which is most commonly a prosthesis.<sup>74</sup>

In this field, metals and their alloys are unavoidable materials in everyday use for making of the fillings, cast post and core systems, crowns and bridges, implant supra-structures, cast partial dentures and metal frameworks.<sup>75</sup> Since these alloys are in direct contact with oral tissues, they must be completely biocompatible i.e. they

should be biologically tolerant (without causing antigen-antibody reaction), biochemically indifferent (remain unchanged in the body without causing any effect on the organism), electrically and magnetically inert (without causing a galvanic current or magnetic field).<sup>28</sup> In Prosthodontics, the incidence of side effects of dental alloys, was calculated to be about 1:400, and about 27% were related to base-metal alloys for removable partial dentures (Co, Cr, Ni) and to noble/gold-based alloys for porcelain fused to metal restorations.<sup>76</sup>

In dentistry, Co–Cr alloys have been used since 1929, mainly for frameworks in removable partial dentures but, in the last decades, application for the manufacture of fixed partial dentures has increased. These alloys are known to exhibit good corrosion properties and offer adequate mechanical properties such as high strength, hardness, high modulus of elasticity and also resistance to tarnish and high temperatures. They are relatively inexpensive when compared to noble alloys and have been shown to be electrochemically more resistant to corrosion than Ni-based alloys.<sup>8, 28, 60</sup> Therefore, in the present study Co-Cr alloys were chosen to be studied.

In these alloys, a chromium oxide film is spontaneously formed, which protects the metal from the surrounding environment and provides resistance to corrosion.<sup>23, 60</sup> However, due to corrosion, metallic medical devices need medium-term replacement, compromising economical national health. Corrosion of dental alloys results in the release of metal ions, which is a prerequisite for the biologic effects to occur.<sup>24</sup> It may leave the restoration esthetically unacceptable because of the formation of pits or colored patinas. The micro-particles released from these cast metal restorations were found in gingival tissues<sup>18</sup> and microbial plaque<sup>19</sup> causing

gingivitis and periodontitis.<sup>24</sup> Therefore, in spite of the recognizable biocompatible characteristics of these alloys, it is mandatory, to go further into the understanding of the chemical and physical phenomena underneath corrosion.<sup>60</sup> That is the purpose of evaluating the corrosion behavior of these alloys. **Giacomelli et al (2004)**<sup>30</sup> found that soluble metal species such as  $\text{CrO}_4^{2-}$  were released into the solution during the Potentiodynamic polarization (PDP).

Apart from the advantages shown by these alloys, the focus of attention is manufacturing method; as the microstructures of these alloys are strongly influenced by the manufacturing processes as well as the chemical composition.<sup>67</sup> The variations in microstructures greatly affect the mechanical<sup>67</sup> and electrochemical properties<sup>8</sup> of the alloys when they are subjected to changes in the oral microenvironment variations.<sup>14</sup> **Alageel et al (2017)**<sup>69</sup> concluded that the polished surfaces of the Conventionally casted (CC) Co-Cr alloys revealed large grains while the surfaces of the Laser sintered (LS) Co-Cr alloys exhibited a fine micro-structural appearance. **Tuna et al (2015)**<sup>8</sup> found that the Co-Cr alloys fabricated by different manufacturing methods (Laser sintering, Milling and casting) showed different corrosion behaviors.

Over the past decades, these metallic restorations have been typically produced by using the conventional lost-wax casting method. The conventional casting method includes prolonged and complex procedures involving various stages and can lead to multiple complications with regard to the quality of casting. To overcome these limitations, new techniques have been introduced. One of these methods includes the computer-aided design/computer-aided manufacturing (CAD/CAM), based on milling i.e. Subtractive manufacturing (SM).<sup>8</sup> SM can create

complete shapes effectively, but at the expense of material being wasted. Approximately 90 percent of a prefabricated block is removed to create a typical dental restoration.<sup>77</sup> Recently, as an alternative, a rapidly emerging, Additive Manufacturing (AM) technique known as Direct Metal Laser Sintering (DMLS) system, has received a significant growth of interest for rapid prototyping and fabrication of various metal components.<sup>27</sup> It is based on a powder-bed process that sinters the materials layer by layer along the path, building a part from a “bath” of metal powder using a laser beam, to produce items based on 3D model data. The advantages of this technology are that no excess material remains, casting defects are eliminated<sup>8, 55</sup> and do not have design constraints as compared to Cast technique.<sup>65</sup> **Koutsoukis T et al (2015)**<sup>61</sup> reported that the Laser sintering technique provides dental prosthetic restorations more quickly and less expensively without compromising their quality compared with restorations prepared by Casting and Milling techniques. **Sing et al (2015)**<sup>57</sup> reviewed the current progress of AM process and observed that SLM fabricated alloy shows a compact homogenous structure with smaller grain size than cast part. This accounts for better corrosion properties in acidic media. Therefore, in this investigation, Co-Cr alloys fabricated by two different manufacturing process i.e., Conventional casting and Laser sintering were chosen.

The measurement of corrosion is complex, and although many investigators have tried to predict corrosion of an alloy by different characterizations such as: OCP (Open circuit potential), PDP (Potentiodynamic Polarization), EIS (Electrochemical impedance spectroscopy), Tafel slopes, Galvanic couplings, Weight loss, etc.; based on its techniques, such predictions are difficult at best. These measurements may be made under a variety of conditions in vitro or, in some cases, in vivo.<sup>78</sup> The most

important fluid in the oral environment is the natural saliva. However, the unstable nature of natural saliva makes it unsuitable for in vitro studies and instead artificial saliva is used.<sup>15</sup> In this work, the corrosion performance of materials was evaluated in artificial saliva (composition as described by Fusayama-Meyer). The solution was freshly prepared before each experiment.<sup>6,8</sup>

Generally, fluoride is added to toothpastes and antiseptic rinses, to strengthen the life-time of teeth. Biomaterials and various surrounding tissues may get exposed to such fluoride containing mediums several minutes every day, depending on usage habits. Literature reports, that the presence of fluoride in saliva increases the tendency of the alloys to corrosion.<sup>25, 75</sup> Studies performed on Ti alloys concluded that fluoride ions present negative influence on the electrochemical behavior of Ti-based alloys due to the complex reaction between Ti and F<sup>-</sup> yielding TiF<sub>6</sub><sup>-2</sup>, a species with high constant formation, originating localized corrosion.<sup>25, 30</sup> However, studies referring to the corrosion behavior of Co-Cr alloys in the presence of fluoride ions are very few. Therefore, in order to verify the influence of fluoride on these alloys, the investigation was performed in artificial saliva containing fluoride. A study conducted by **Reclaru and Meyer (1998)**<sup>20</sup> to find the effect of fluoride on Co-Cr alloys, concluded that there is a decrease in the corrosion resistance of the alloy in a fluoride environment. **Huang (2003)**<sup>25</sup> found that the protectiveness of the passive film formed on Ti alloy was destroyed by fluoride ions when the NaF concentration was increased up to 0.1%.<sup>25</sup> **Yang et al (2014)**<sup>16</sup> examined the effect of fluoride concentration (0, 0.05, 0.1 and 0.2%) on ion release from Co-Cr-Mo alloy specimens in an artificial saliva solution and found the highest elemental release at 0.2 % NaF. The same percentage of fluoride was used in the present study.

When Co-Cr alloys are used in the oral cavity, a comprehensive knowledge of their effect on the surrounding tissues is required, therefore the electrochemical behavior of these alloys should not only be studied in artificial saliva but also in the most unfavorable environment such as aggressive pH.<sup>30</sup> **Giacomelli et al (2004)**<sup>30</sup> concluded that electrochemical properties are markedly influenced by solution pH and temperature. Therefore, to evaluate the stability of these alloys in test solutions, the corrosion testing was performed at pH 5.3 and temperature  $37 \pm 1^\circ\text{C}$ .<sup>8</sup> **Khan et al (1999)**<sup>21</sup> studied and compared the *in vitro* corrosion of three Ti alloys in various protein solutions with phosphate-buffered saline (PBS = control) at different pHs (5, 7.4 and 9) and concluded that corrosion was higher at low pH.

The difference in corrosion behavior of metals and alloys is due to the spontaneous formation of a thin, compact layer of oxides called the passive layer.<sup>44</sup> Corrosion disintegrates these surface oxides films under highly reductive conditions, although such conditions are not usually found in the mouth. Paradoxically, overuse of the most frequent preventive means in dental medicine and surface application of fluorides, can cause the self-formed protective film to become less stable and eventually a breakdown of the film may occur.<sup>15, 34</sup> **Hanawa et al (2001)**<sup>23</sup> studied the Co-Cr-Mo alloys in various environments and found that the surface oxide was about 2.5 nm thick and contained a large amount of  $\text{OH}^-$ . **Robin and Meirelis (2009)**<sup>79</sup> observed that presence of fluoride in saliva enhanced porosity of this oxide film. **Xin et al (2014)**<sup>58</sup> concluded that the thickness of oxide layer of DMLS alloys was greater than cast alloys, both before and after porcelain firing.

Two test conditions were performed, 20 samples were tested without any storage and other 20 samples were stored for 2 months followed by testing. As already discussed, the corrosion resistance of the alloys is dependent on its protective oxide film.<sup>16</sup> It is unlikely that the passive layers on these alloys will be broken down electrochemically in the corrosive environment. However, the integrity of the passive layer can be influenced by wear<sup>21</sup> and fluoride ions.<sup>15, 16, 80</sup> It is therefore important to investigate the behavior of these alloys in a corrosive environment after storage (immersion). Several investigations were done on metal ion release of alloys after immersion of samples for 7 days<sup>16</sup>, 15 and 30 days<sup>14</sup> and at different occasions from 1-30 days concluding that dissolution is dependent on nature of solution and time of immersion.<sup>5, 28, 54</sup> **Mareci et al (2005)**<sup>33</sup> studied the corrosion behavior of Ni- and Co-based alloys and concluded that the maintenance time (24 hrs and 7 days) of the alloy decreases the corrosion rate of alloys due to their passivation in solution. Therefore, this study was an attempt to compare the corrosion behavior of Co-Cr alloys after long time exposure to solutions.

The surface state is an important factor in the corrosion behavior of dental alloys. A study conducted by **Kaneko et al (2000)**<sup>22</sup> found that mirror finished samples showed the highest resistance to corrosion in corrosive electrolytes. **Mimura and Miyagawa (1996)**<sup>81</sup> found that cast titanium was less resistant to corrosion due to its inferior surface state. Therefore, all the samples were abraded using series of emery papers (#150, 400, 600, 800, 1200 and 1500) and cloth polishing smeared with alumina was performed to get the perfect mirror polishing using a grinder-polisher machine.

Many corrosion phenomena can be explained in terms of electrochemical reactions and the electrochemical techniques can be used to study these phenomena. Measurements of current-potential relations under carefully controlled conditions can yield information on corrosion rates, coatings and films, passivity, pitting tendencies and other important data.<sup>82</sup> Tafel extrapolation and polarization resistance are two methods to measure corrosion rates. The electrochemical method consisting of polarization curve recording is of particular interest.<sup>33</sup> In the present investigation also, these curves were obtained (PDP plots) and corrosion rate was determined using Tafel extrapolation technique. The PDP was performed at a scan rate of  $0.20 \text{ mV s}^{-1}$  (as per ASTM standard). **Ameer et al (2004)**<sup>29</sup> concluded that the  $10 \text{ mV/min}$  ( $\sim 0.20 \text{ mV s}^{-1}$ ) is the best scan rate because at this value the corrosion rate is very low when compared at  $50 \text{ mV /min}$ .

Electrochemical behavior of a corroding metal can be characterized by determining polarization parameters, such as Corrosion potential ( $E_{\text{corr}}$ ) and Corrosion current density ( $I_{\text{corr}}$ ). Then the Tafel behavior can be disclosed by a polarization curve ( $E \text{ vs. } \log i$ ). Evaluation of these parameters leads to the determination of the Corrosion rate as  $I_{\text{corr}}$  which is often converted into Faradaic corrosion rate. The Corrosion rate ( $C_R$ ) of an alloy can be quantified by measuring the current flow associated with metal oxidation.<sup>8, 60</sup> This electrochemical process for determining  $C_R$  has an advantage over the determined  $C_R$  by weight loss, since the latter is a time-consuming process, which may lead to unsatisfactory results when  $C_R$  changes with time. Instead, a polarization curve is readily obtained and it can offer a practical method for characterizing electrochemical parameters.<sup>83</sup> In this study, the same method was followed for determining  $E_{\text{corr}}$  and  $I_{\text{corr}}$  using PDP curves, which was

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obtained by using potentiostat attached to the computer. **Huang (2003)**<sup>25</sup> also evaluated the corrosion resistance of Ti alloys using corrosion parameters, including  $E_{\text{corr}}$  and  $I_{\text{corr}}$  obtained from the PDP curves. **Giacomelli et al (2004)**<sup>30</sup> also studied the corrosion behavior of a Co-Cr-Mo biomaterial used as dental prosthesis using electrochemical techniques i.e. (OCP and PDP) in artificial saliva, artificial saliva with modified temperature (7 °C – 47 °C) and pH (1.4 – 13.4), and containing fluoride (1500 ppm). Similarly, **Hsu et al (2005)**<sup>32</sup> studied the electrochemical properties ( $I_{\text{corr}}$  and  $E_{\text{corr}}$ ) of Co-Cr-Mo implant alloys in biological solutions (joint fluid, serum and urine).

$E_{\text{corr}}$  is the corrosion potential at which the rate of oxidation is exactly equal to the rate of reduction, which determines the thermodynamic stability of the alloy.  $I_{\text{corr}}$  i.e., current density, is the point of intersection of anodic and cathodic slopes on the Tafel plot. The corrosion rate depends on the kinetics of both anodic (oxidation) and cathodic (reduction) reactions; and is related directly to  $I_{\text{corr}}$ . Therefore, the more the  $I_{\text{corr}}$  the more is the corrosion rate i.e. higher corrosion and dissolution of sample.<sup>82, 84</sup>

It can be observed from the PDP plots (Annexure) that all the PDP curves are similar in nature indicating no change in the behavior of both the alloys manufactured by different methods, in different test solutions and different test conditions. The cathodic part of the plots have a curvilinear arc indicating the cathodic reaction to be under the activation control. Anodic part of the plot shows;

- a. Increase in corrosion current density ( $I_{\text{corr}}$ ) i.e. active region
- b. Straight lines above 0.3  $V_{\text{SCE}}$  (voltage w.r.t  $\text{SCE}$ ) showing onset of passivation i.e. passive region

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- c. Sudden increase in the corrosion current density indicating the onset of pits in the material i.e. transpassive region

A Study conducted by **Huang (2003)**<sup>25</sup> also found that the PDP plots showed active to passive transition at NaF concentration of < 0.5 %.

#### **Potentiodynamic polarization (PDP):-**

1. **Between subgroups:-** Comparisons between manufacturing methods i.e. samples either fabricated by Casting (C) or DMLS (D), in both the test solutions: AS and ASF, at test conditions N and S i.e. between Div's CN-DN, CNF-DNF, CS-DS and CSF-DSF.

**$E_{\text{corr}}$ :** - The  $E_{\text{corr}}$  of all the samples of subgroups D has shifted more towards noble direction when compared to the all the respective samples of subgroups C as mentioned in Table 1. This shift of subgroups D towards noble direction indicates that these DMLS samples are thermodynamically more stable and have a tendency to passivate by forming Cr oxide film, compared to cast samples. Two way ANOVA test reveals statistically significant results between subgroups as mentioned in Table 2 for test condition N ( $p < 0.0001$ ) and Table 3 for test condition S ( $p < 0.0001$ ).

**$I_{\text{corr}}$ :** -The  $I_{\text{corr}}$  of all the samples of subgroups D is less than that of respective samples of subgroups C as mentioned in Table 4. This decrease in  $I_{\text{corr}}$  of DMLS samples indicate that the corrosion rate of these samples is less than cast samples indicating less corrosion/ dissolution, irrespective of any electrolyte. Two way ANOVA test reveals statistically significant results between subgroups as mentioned in Table 5 for test condition N ( $p < 0.046$ ) and Table 6 for test condition S ( $p < 0.002$ ).

**Tuna et al (2015)**<sup>8</sup> found similar results, wherein the  $I_{\text{CORR}}$  of milled and laser sintered Co-Cr samples was less than cast samples and concluded that corrosion rate of cast samples was higher. **Sing et al (2015)**<sup>65</sup> concluded that casting alloys show greatest risk of corrosion under acidic conditions than SLM (Selective laser melted) or EBM (Electron beam melted) alloys.

The results of present study revealed that the corrosion has occurred in samples manufactured by both the methods. However, the corrosion occurred in DMLS samples is very less than cast samples. The reason for corrosion to occur in DMLS processed samples could be due to differences in factors such as; scan spacing, laser power, scan rate or scan thickness affecting the sintering procedure.<sup>61</sup> Also as previously discussed, the cast samples have casting defects (different types of porosities or impurities); such defects are eliminated in samples fabricated by DMLS technology. These defects can be the anodic sites for the corrosion to occur leading to poor corrosion behavior in cast samples.

**Galo et al (2012)**<sup>49</sup> stated that the effect of artificial saliva on the corrosion of dental alloys is strongly dependent on alloy composition. Therefore, one of the reasons for improved performance of DMLS alloys could also be because of the addition of tungsten (W), which is known to improve the corrosion properties of Co-Cr alloys and reduces chromium-depleted inter-metallic areas.<sup>55</sup> The microstructure of the alloys also strongly influence the corrosion properties.<sup>8</sup> **Lucia D (2017)**<sup>70</sup> showed that in DMLS technique, Co-Cr particles are joined not only within layers but also between different layers making them more compact and fused. This could be one of the reasons for superior corrosion performance of DMLS samples.

2. **Between groups:-** Comparisons between presence and absence of fluoride i.e. Control (AS) and Experimental (ASF) groups at test conditions N and S.

**$E_{\text{corr}}$ :** -The  $E_{\text{corr}}$  of all the samples of AS group shifted more towards noble direction compared to the respective samples of ASF group regardless of any test condition N or S, as mentioned in Table 1. This indicates the thermodynamically stable behavior of the alloy in the absence of fluoride. Two way ANOVA test reveals statistically significant results between groups as mentioned in Table 2 for test condition N ( $p < 0.0001$ ) and Table 3 for test condition S ( $p < 0.0001$ ).

**$I_{\text{corr}}$ :** - The  $I_{\text{corr}}$  of all the samples of group ASF was greater than respective samples of group AS, at test condition N or S as mentioned in Table 4. This indicates that the corrosion rate (dissolution of metal) of samples in the presence of fluoride is greater, i.e. samples in fluoride solution will corrode more compared to samples without fluoride. Two way ANOVA test reveals statistically significant results between subgroups as mentioned in Table 5 for test condition N ( $p < 0.005$ ) and Table 6 for test condition S ( $p < 0.006$ ).

A study conducted by **Huang (2003)**<sup>25</sup> found that increasing the NaF concentration (from 0% to 0.5%) led to a significant increase in the  $I_{\text{corr}}$  and a significant shift of  $E_{\text{corr}}$  away from noble direction. **Kocijan et al (2004)**<sup>31</sup> studied the composition of the passive layers of Co-based alloys in simulated physiological solution (SPS), with and without the complexing agent EDTA and found that, in presence of EDTA, the content of Co-, Ni- and Mo- oxide in the passive layer is lower indicating increased solubility associated with higher stability constants for complexes of metal cations with EDTA. **Al Subari et al (2013)**<sup>50</sup> concluded that the

presence of khat extract in artificial saliva led to accelerate the corrosion of Ni-Cr alloys and this may be due to the presence of fluoride, amino acids, tannic acid or ascorbic acid in khat. In the present study also, the aggressive nature of fluoride on the developed passive layer might be the reason for poor corrosion behavior in solutions containing NaF.

**3. Between test conditions:-** Comparisons between test conditions non-stored (N) and stored (S)

**$E_{\text{corr}}$ :** - The  $E_{\text{corr}}$  of samples at test condition S has significantly shifted towards noble direction compared to the samples at test condition N, as mentioned in Table 1.

**$I_{\text{corr}}$ :** - The  $I_{\text{corr}}$  of the samples at test condition S is significantly less than the samples at test condition N, as mentioned in Table 4.

A study conducted by **Mareci et al (2005)**<sup>33, 43</sup> concluded that the  $E_{\text{corr}}$  of the alloy shifts towards positive direction and the  $I_{\text{corr}}$  of the alloy decrease with the maintenance or immersion time (24 h and 7 days) due to their passivation in solution. **Giacomelli et al (2004)**<sup>30</sup> observed a corrosion resistant behavior in acid solutions due to the formation of stable molybdenum oxides ( $\text{MoO}_3$  and  $\text{MoO}_2$ ).

In the present study also, the reason for obtaining comparatively stable corrosion behavior of the samples at stored test condition (S), could have been because of the formation of the protective oxide film that might have resisted the alloy from corrosive.

**4. Comparisons between all Divisions:-**

The  $E_{\text{corr}}$  shifted to a noble direction in the following descending order; as mentioned in Table 1 and Column chart 1

$$DS > DSF > CS > CSF > DN > CN > DNF > CNF$$

The  $I_{\text{corr}}$  was observed in the following ascending order; as mentioned in Table 4 and column chart 2

$$DS < DSF = CS < DN \leq CSF < CN < DNF < CNF$$

The respective orders of  $E_{\text{corr}}$  and  $I_{\text{corr}}$  of different divisions as presented above indicates that the DMLS samples in stored conditions showed excellent corrosion behavior in the absence of fluoride, whereas the poorest corrosion behavior was observed by cast samples in fluoride solution. At the same time, it should also be noted, that DMLS samples even in the presence of fluoride showed better corrosion behavior than cast samples in the absence of fluoride.

From the study performed, it can be summarized that the corrosion rate of the cast alloys is greater than that of DMLS alloys. Presence of fluoride in the test electrolyte increases the corrosion rate of these alloys.

Therefore, the null hypothesis is rejected and alternate hypothesis is accepted i.e. both the factors, i.e. fluoride concentration and manufacturing methods show a statistically significant difference in corrosion behavior of Co-Cr alloys and this difference is not by chance.

Almost all the restorations were earlier fabricated using lost-wax technique but the most modern DMLS technology provide better corrosion behavior. This

technology provides a better future in terms of less corrosion rate, which is more biocompatible for surrounding oral tissues as compared to the conventional casting. Therefore this technique should be routinely advisable for fabricating prosthesis.

Fluoride-containing toothpastes and mouthwashes are beneficial to the oral health for multiple purposes but, other than the advantages shown by fluoride, it has de-merits of corroding the metal restorations in the oral cavity.

After recent insertion of the prosthesis, the alloy is more prone to corrosion in fluoride containing oral media. However, on standing a protective oxide film is formed on the surface of the metal that resists corrosion to an extent, establishing a balance between electrolytes with the amount of corrosion in relation to time. Therefore, during the long-term use of the metal prosthesis, both the patient and doctor should carefully use the fluoride containing products to minimize unexpected damage to the prosthesis.

**Clinical implications:-**

1. Co-Cr alloys are commonly used for dental prostheses, but corrosion of these alloys may alter the form of the prosthesis creating a rough surface which can be more retentive for plaque and debris. This may weaken the prosthesis and damage the adjacent tissues. Therefore it is essential to study, the corrosion behavior of these alloys in the clinical usage.
2. The corrosion behavior of Co-Cr dental alloys is dependent on fabrication method. Alloys fabricated by DMLS system are preferable to conventional casting for Co-Cr alloys.
3. Presence or absence of fluoride also influences the corrosion behavior of these alloys fabricated by different methods. The presence of fluoride in the oral cavity can accelerate corrosion, regardless of processing methods.

4. Irrespective of fabrication method and presence or absence of fluoride, the storage condition (Immersion time) leads to the formation of a protective oxide layer that is resistant to corrosion. Therefore, understanding the behavior of these alloys on a long run is important to promote a better oral health.

**Limitations:-**

In this study, the corrosion tests were performed using Potentiodynamic polarization method and the corrosion behavior was studied. The study was designed and carried out with utmost accuracy. However, the present study has certain limitations which are enlisted below.

1. As this is in vitro study, the oral conditions could not be simulated.
2. Scanning electron microscopy (SEM) examination of the samples to evaluate microstructure of these alloys was not performed.

**Scope for further studies:-**

1. X-ray photometric spectroscopy (XPS) analysis can be done to further determine the structure and thickness of the surface oxide film.
2. Electrochemical Impedance Spectroscopy (EIS) measurements can be done to determine the nature of a passive film.
3. ICP-AES (Inductively coupled plasma- atomic emission spectroscopy) can be done to determine the release of metal ions.
4. SEM analysis can be done to determine the surface condition after corrosion.

# Summary

*If you cannot do great things, do small things in a great way*

The present investigation was done with the aim to evaluate and compare the corrosion rate of Conventional and Direct Metal Laser Sintered (DMLS) Co-Cr dental alloys in fluoride solution.

In this study, Co-Cr samples were fabricated with 2 different manufacturing methods: the conventional casting using lost-wax technique and Direct Metal Laser Sintering (DMLS). For the purpose of an investigation, 40 disk-shaped samples of 5mm diameter and 3 mm thickness were fabricated.

The samples were mounted, finished and polished using standardized methods. They were divided into 2 groups, i.e. Control and Experimental groups. Two test conditions were performed, viz. testing the samples without any storage (N) and

storage for two months (S) followed by testing. The samples of the control group were immersed and tested in artificial saliva solution (AS) while that of experimental groups were immersed and tested in artificial saliva solution containing 0.2% NaF (ASF). The solutions were buffered with lactic acid to keep at pH 5.3 and temperature was maintained at  $37\pm 1^\circ\text{C}$  using; oven (during storage) and thermostat (during testing).

The instrument “Potentiostat (BIOLogic)” connected to a computer was used to examine the corrosion behavior of test alloys (Cast and DMLS) in AS and ASF solutions. The conventional three-electrode system was used for corrosion testing and PDP plots were obtained. The  $E_{\text{corr}}$  and  $I_{\text{corr}}$  values were extracted from the PDP plots using Tafel extrapolation method.

$E_{\text{corr}}$  is the corrosion potential at which the rate of oxidation is exactly equal to the rate of reduction.  $I_{\text{corr}}$  i.e., current density, is the point of intersection of anodic and cathodic slopes. The corrosion rate depends on the kinetics of both anodic (oxidation) and cathodic (reduction) reactions; and is related directly to  $I_{\text{corr}}$ .

The results revealed that corrosion behavior of the Co-Cr samples manufactured by DMLS technique was better than those of the cast samples. The samples tested in fluoride containing artificial saliva solution showed poor corrosion performance than the ones not containing fluoride. Amongst the two test conditions employed, the samples stored for two months showed notably higher corrosion behavior than the ones not stored.

# *Conclusion*

*Today a reader, tomorrow a leader*

The aim of the study was to evaluate and compare the corrosion rate of Conventional and Direct Metal Laser Sintered (DMLS) Co-Cr dental alloys in fluoride solution.

Within the limitations of the study, following conclusions can be drawn;

1. Compared with cast alloy, the DMLS alloy showed better corrosion behavior, irrespective of test solutions or test conditions.
2. The presence of fluoride in the solutions significantly affected the corrosion behavior of both DMLS and cast Co-Cr alloys.

3. Test condition had a significant influence on corrosion behavior of the alloys. The samples stored at a storage period of two months showed notably superior corrosion performance compared to the samples not stored in test solution before corrosion testing.

# *Bibliography*

*Review your goals twice everyday in order to be focused on achieving them*

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**Table 1: Descriptive statistics of mean corrosion potential ( $E_{corr}$ ) for groups AS and ASF; and subgroups C and D at test conditions N and S.**

Test condition	Control group (AS)				Experimental group (ASF)			
	N	Cast (Subgroup C)	n	DMLS (Subgroup D)	n	Cast (Subgroup C)	n	DMLS (Subgroup D)
		$E_{corr}$ (mV)		$E_{corr}$ (mV)		$E_{corr}$ (mV)		$E_{corr}$ (mV)
<b>Non-stored- N</b> [M ± SD]	5	-179.23 ± 2.66	5	-151.37 ± 0.78	5	-259.37 ± 2.74	5	-236.47 ± 1.49
<b>Stored - S</b> [M ± SD]	5	-23.35 ± 1.33	5	-8.22 ± 3.47	5	-37.06 ± 1.99	5	-18.04 ± 2.51
<b>P-value*</b>		< 0.0001 (HS)		< 0.0001 (HS)		< 0.0001 (HS)		< 0.0001 (HS)

\*Obtained using paired t-test; HS: Highly significant

**Table 2: Two-way ANOVA for mean corrosion potential ( $E_{corr}$ ):– test-condition**

N

$E_{corr}$ (mV) (test-condition N)	Sum of Squares	DF	Mean Square	F	P-value*
<b>Between groups</b>	34133.049	1	34133.049	12750.256	<0.0001 (S)
<b>Between subgroups</b>	3220.7981	1	3220.7981	1203.1156	<0.0001 (S)

\*Calculated using Two-way ANOVA; S: Significant

**Table 3: Two-way ANOVA for mean corrosion potential ( $E_{corr}$ ):– test-condition S**

$E_{corr}$ (mV) (test-condition S)	Sum of Squares	DF	Mean Square	F	P-value*
<b>Between groups</b>	696.2	1	696.2	110.508	<0.0001 (S)
<b>Between subgroups</b>	1479.2	1	1479.2	234.794	<0.0001 (S)

\*Calculated using Two-way ANOVA; S: Significant

**Table 4: Descriptive statistics of mean corrosion current density ( $I_{corr}$ ) for groups AS and ASF; and subgroups C and D at test conditions N and S.**

Test condition	Control group (AS)				Experimental group (ASF)			
	n	Cast (Subgroup C)	n	DMLS (Subgroup D)	n	Cast (Subgroup C)	n	DMLS (Subgroup D)
		$I_{corr}(\mu A/cm^2)$		$I_{corr}(\mu A/cm^2)$		$I_{corr}(\mu A/cm^2)$		$I_{corr}(\mu A/cm^2)$
Non-stored- N [M $\pm$ SD]	5	0.15 $\pm$ 0.02	5	0.06 $\pm$ 0.02	5	0.21 $\pm$ 0.07	5	0.17 $\pm$ 0.11
Stored - S [M $\pm$ SD]	5	0.02 $\pm$ 0.01	5	0.01 $\pm$ 0.01	5	0.07 $\pm$ 0.03	5	0.02 $\pm$ 0.01
<b>P-value*</b>		0.00015 (S)		0.0084 (S)		0.0269 (S)		0.0411 (S)

\*Obtained using paired t-test; S: Significant

**Table 5: Two-way ANOVA for mean corrosion current density ( $I_{corr}$ ):- test-condition N**

$I_{corr}$ ( $\mu A/cm^2$ ) (test-condition N)	Type III Sum of Squares	DF	Mean Square	F	P-value*
Between groups	0.059	1	0.059	10.609	0.005 (S)
Between subgroups	0.006	1	0.006	1.153	0.046 (S)

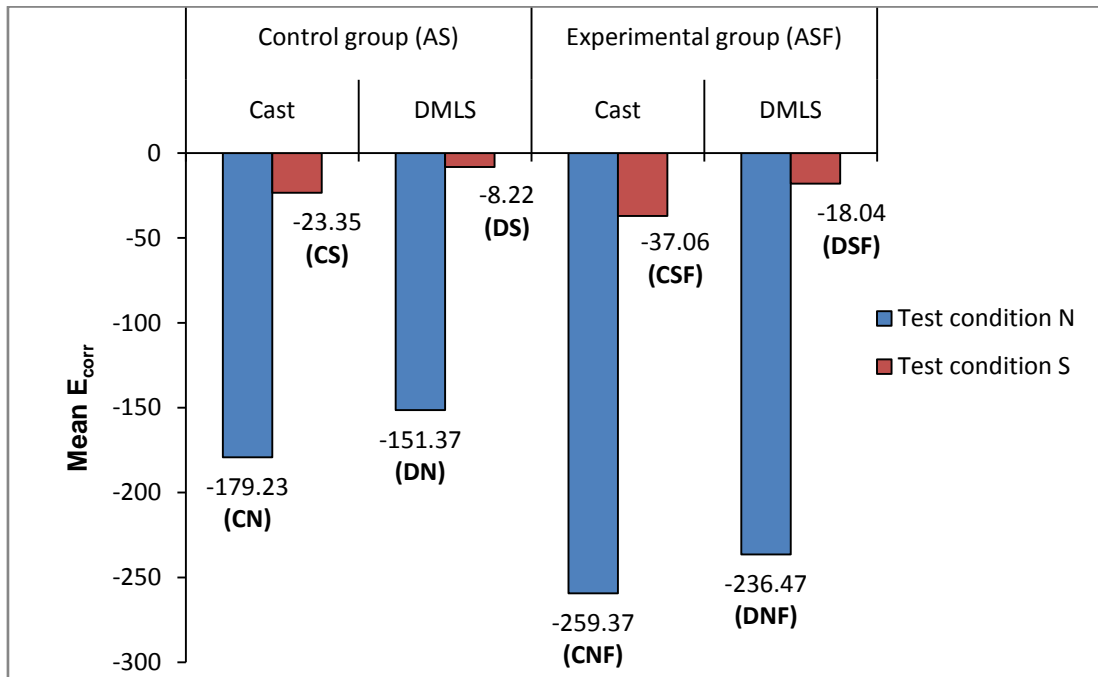
\*Calculated using Two-way ANOVA; S: Significant

**Table 6: Two-way ANOVA for mean corrosion current density ( $I_{corr}$ ):- test-condition S**

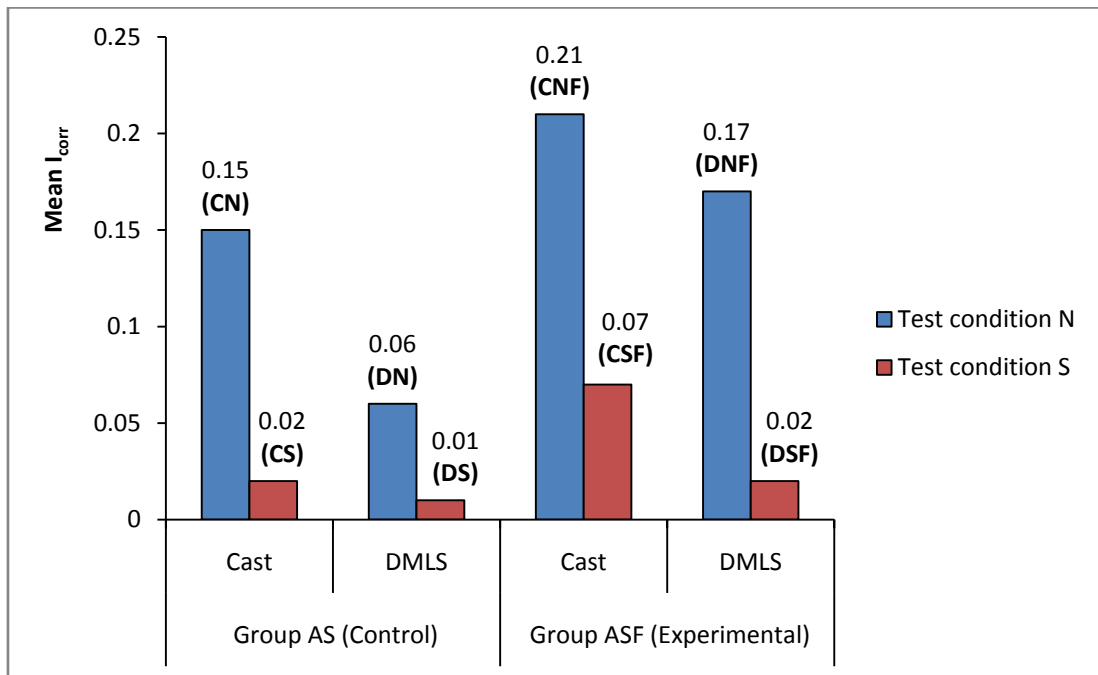
$I_{corr}$ ( $\mu A/cm^2$ ) (test-condition S)	Type III Sum of Squares	DF	Mean Square	F	P-value*
Between groups	0.003	1	0.003	9.941	0.006 (S)
Between subgroups	0.005	1	0.005	13.235	0.002 (S)

\*Calculated using Two-way ANOVA; S: Significant

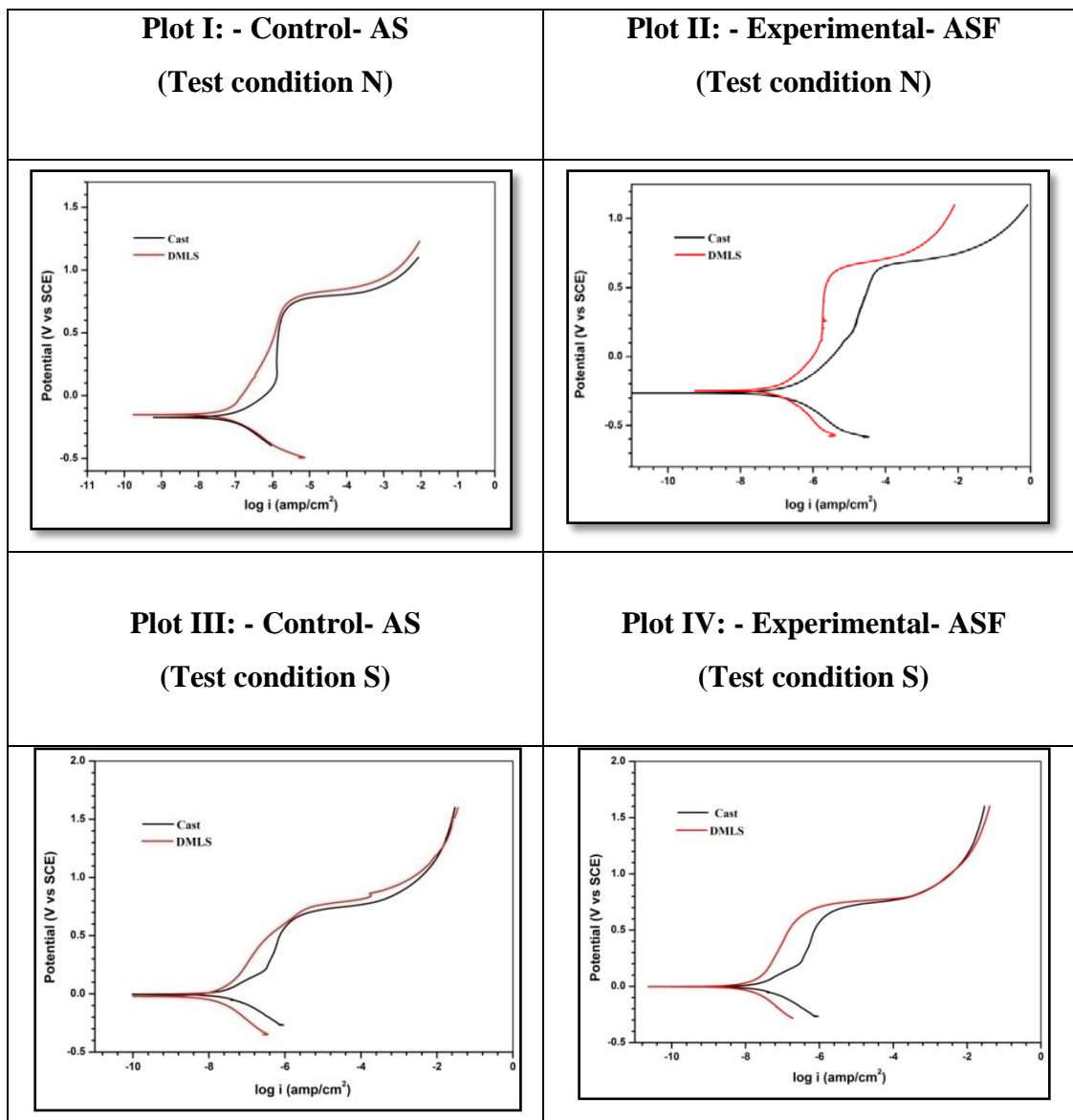
**Column chart 1: Mean corrosion potential ( $E_{\text{corr}}$ ) of samples for groups AS and ASF; and subgroups C and D at test conditions N and S.**



**Column chart 2: Mean corrosion current density ( $I_{\text{corr}}$ ) of samples for groups AS and ASF; and subgroups C and D at test conditions N and S.**



## PDP PLOTS



## MASTER CHART

Sr.no.	Div. CN		Div. CNF	
	$E_{\text{corr}}$ (mV)	$I_{\text{corr}}$ ( $\mu\text{A}/\text{cm}^2$ )	$E_{\text{corr}}$ (mV)	$I_{\text{corr}}$ ( $\mu\text{A}/\text{cm}^2$ )
1.	-179.340	0.161	-259.883	0.211
2.	-180.151	0.140	-262.149	0.114
3.	-178.514	0.151	-258.552	0.201
4.	-179.125	0.180	-261.175	0.316
5.	-178.998	0.142	-255.102	0.213

Sr.no.	Div. DN		Div. DNF	
	$E_{\text{corr}}$ (mV)	$I_{\text{corr}}$ ( $\mu\text{A}/\text{cm}^2$ )	$E_{\text{corr}}$ (mV)	$I_{\text{corr}}$ ( $\mu\text{A}/\text{cm}^2$ )
1.	-151.250	0.061	-235.515	0.111
2.	-151.580	0.095	-237.88	0.21
3.	-150.121	0.072	-238.121	0.092
4.	-152.212	0.059	-236.115	0.35
5.	-151.680	0.03	-234.712	0.08

Sr.no.	Div. CS		Div. CSF	
	$E_{\text{corr}}$ (mV)	$I_{\text{corr}}$ ( $\mu\text{A}/\text{cm}^2$ )	$E_{\text{corr}}$ (mV)	$I_{\text{corr}}$ ( $\mu\text{A}/\text{cm}^2$ )
1.	-23.88	0.026	-37.205	0.065
2.	-24.998	0.012	-34.561	0.112
3.	-22.149	0.039	-40.102	0.022
4.	-21.83	0.014	-36.801	0.059
5.	-23.911	0.02	-36.611	0.088

Sr.no.	Div. DS		Div. DSF	
	$E_{\text{corr}}$ (mV)	$I_{\text{corr}}$ ( $\mu\text{A}/\text{cm}^2$ )	$E_{\text{corr}}$ (mV)	$I_{\text{corr}}$ ( $\mu\text{A}/\text{cm}^2$ )
1.	-8.258	0.014	-18.65	0.018
2.	-4.132	0.021	-17.404	0.024
3.	-8.198	0.006	-20.801	0.02
4.	-6.86	0.01	-14.11	0.01
5.	-13.65	0.016	-19.235	0.008