COMPARATIVE EVALUATION OF SHEAR BOND STRENGTH OF CAST AND DIRECT METAL LASER SINTERED Co-Cr ALLOY TO PORCELAIN WITH THE EFFECT OF SURFACE TREATMENTS - AN IN VITRO STUDY

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CERTIFICATE

This is to certify that the dissertation titled "**COMPARATIVE EVALUATION OF SHEAR BOND STRENGTH OF CAST AND DIRECT METAL LASER SINTERED Co-Cr ALLOY TO PORCELAIN WITH THE EFFECT OF SURFACE TREATMENTS - AN IN VITRO STUDY**" is a bonafide record work done by **Dr. RAJKUMAR E.** under our guidance and to our satisfaction during his post graduate study period between 2010 - 2013.

This dissertation is submitted to **THE TAMILNADU Dr. M.G.R. MEDICAL UNIVERSITY**, in partial fulfillment for the degree of **MASTER OF DENTAL SURGERY – PROSTHODONTICS AND CROWN AND BRIDGE, BRANCH I.** It has not been submitted (partial or full) for the award of any other degree or diploma.

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ABSTRACT

PURPOSE OF STUDY

The present in vitro study was conducted for the comparative evaluation of shear bond strength of cast Co-Cr alloy and the direct metal laser sintering (DMLS) Co-Cr alloy to dental porcelain with the effect of sand blasting and laser etching surface treatments.

MATERIALS AND METHODS

Twenty cast Co-Cr alloy and twenty DMLS Co-Cr alloy specimens were fabricated and divided into four groups (Group I, II, III & IV). The alloy surfaces were surface treated with sand blasting and laser etching procedures. Dental porcelain was applied on cast and DMLS Co-Cr alloy. Ten test samples were prepared for each group for bond strength comparison. All samples were tested for shear bond strength in Universal testing machine and the results were calculated for statistical analysis. The samples were qualitatively analysed by SEM and EDX analysis to correlate the results with above.

RESULTS

The highest shear bond strength value was obtained with laser sintered Co-Cr alloys-ceramic test samples after laser etching (Group IV- 72.38 ± 0.89 MPa) followed by cast Co-CR alloy-ceramic test samples after laser etching (Group II- 72.27 ± 0.91MPa), followed by laser sintered Co-Cr alloy- ceramic test samples after sand blasting (Group III- 71.01± 1.97 MPa) and least by cast Co-Cr alloy- ceramic after sand blasting (Group I- 70.21±2.69 MPa)

Group IV >Group> II >Group III> Group I

CONCLUSION

The DMLS metal ceramic system exhibited a bonding strength that exceeds the requirement of ISO 9691:1999. Surface treatment with laser etching on the surface of DMLS Co–Cr alloy improved the bond strength when compared to sand blasting. The new laser sintering technique for Co-Cr alloy (DMLS) seems to be an alternative technique to conventional casting of dental alloys for porcelain fused to metal restorations.

KEY-WORDS

Laser sintering, laser etching, DMLS, Sand blasting, Shear bond strength.

INTRODUCTION

Metal ceramic restorations are considered a predictable option in fixed prosthodontics, despite the newer developments and increase in use of all-ceramic systems.[26] The frequent problems associated with all ceramic restorations are chipping of the veneering porcelain and fracture of the connector area in long span fixed partial dentures (FPDs).[25,38] This has led to the revival of porcelain fused to metal (PFM) restorations as innovative fabricating methods and newer materials in metallurgical science and compatible porcelain systems have made the PFM restoration more definitive. Metal ceramic restorations combine the strength of metal and esthetics of porcelain to produce an esthetic and functional result. They present less clinical failures as opposed to all ceramic restorations.[10,27,36]

Various types of alloys like noble and base metal alloys are used for the fabrication of the substructures of metal ceramic restorations. Noble metal casting alloys, due to their biocompatibility and the ability to form good metal-ceramic bond were considered as ideal metal substructures for PFM restorations,[1] but considerable increase in the price of gold resulted in the use of non-precious alloy system for PFM restorations.[9,24,28,33,43]

The favorable mechanical properties of non-precious metal alloy allows for restorations with less thickness and more rigidity.[8,9,43] The rigid nature of these alloys is directly attributed to their high elastic moduli and this property allows the possibility of fabricating long-span fixed prostheses, as they undergo less flexure than do similar prostheses fabricated from noble metal alloys, with less likelihood of fracture of the brittle dental porcelain component.[21,28,33]

Non-precious alloys especially Nickel-Chromium were used extensively as metal substructures for FPD prostheses. The allergenic potential of Nickel and Beryllium which are mainly present in these alloys has prompted the consideration of other base metal alloys, such as Titanium alloys and Cobalt-Chromium.[26] The deterrents to the use of titanium in dentistry have been its high melting temperature and reactivity, rendering the casting operation very difficult and necessitating special melting procedures, mold material and equipment.[3,15]

Cobalt-Chromium alloys possess higher melting temperature and this makes the melting and the casting procedure more technique sensitive and in addition the castings obtained from Co-Cr alloys are difficult to finish, compared to noble alloys. However, such disadvantages may be minimized due to introduction of newer processing technology, improved material properties, and metal substructure design.[7,40] Electrochemical studies show that Co-Cr alloys are more resistant to corrosion than Ni-Cr. Hence the use of the more biocompatible Co-Cr based alloys has been suggested nowadays as metal substructures for PFM restorations, since they have shown excellent marginal integrity and minimal adverse reactions.[47]

There are various techniques available to fabricate chrome-cobalt substructures, like conventional lost-wax technique, milled wax with lost-wax method, milled Co-Cr (CAD-CAM milling) and direct metal laser sintering (DMLS). Involvement of tedious lab procedures, dimensional alterations of the wax pattern and solidification shrinkage during castings have led to the utilization of CAD-CAM and direct metal laser sintering techniques.[35] CAD-CAM milling does not require making of conventional impression of prepared teeth or the involvement of dental assistants. It produces restorations free of porosity and it requires just a single appointment for placement of the restoration.[1,14] However limitations still exists with this technique, as undercuts in the cervical areas of the prepared teeth are not captured during optical impression making and it also involves expensive armamentarium. Milling of base metal alloys results in a high loss of time and rapid wear of milling tools.[44]

Direct metal laser sintering is a CAD-CAM based technique in which metal copings can be designed and fabricated using Co-Cr. Alloy powder used in this technique has less percentage of molybdenum, when compared with the Co-Cr alloy used in conventional casting. This process builds up each coping in a series of successive thin layers (0.020 mm). A high power laser beam is focused on to a bed of powdered metal and these areas fuse into thin solid layer and another layer of powder is laid down over this and the next slice of coping is fused to the previous layer, until the coping is completed. It is a promising new technology which may replace conventional casting of base metal alloys. The advantages of this system as claimed by the manufacturer are reduction of unit production cost compared to the conventional lost wax casting technique, the ability to manufacture up to 90 units in a single operation, ease of use, accuracy of parts produced without much retained porosity, simplified post-processing procedures, improved physicochemical characteristics[1, 51] and near full density objects with complex geometries can be produced.[51]

The clinical success of the metal-ceramic restorations depends primarily on the strength and integrity of the adhesion between the metal and porcelain at the interface, the most susceptible site for occurrence of cracks.[1] The cracks generally progress through the metal-ceramic interface or through the veneering porcelain resulting in either chipping or delamination of the veneering porcelain, which may finally end up with esthetic and biological complication.[1,50]

The bonding at the metal-ceramic interface is attributed to van-der-Waal's forces, mechanical interlocking between both materials, compressive bonding forces and chemical bonds between the ceramic and oxide layer of alloy, with chemical bonding being the main determinant of union, as characterized by the direct transfer of electrons between the oxygen in the vitreous part of ceramic and oxidation of metal.[10,26,41]

It is essential to have adequate bond strength between the alloy and porcelain in metal-ceramic restorations.[1] There are several surface treatments available in order to improve the bond strength between the metal and ceramics. The main purpose of all these surface treatments is to increase the wettability of the metal by porcelain and also to control the formation of oxide layer. These methods include, air abrasion, acid etching, application of bonding agent, degasification, heat treatment, mechanical retention obtained by roughening with carbide burs and diamond mounted tips and laser etching.[18,20,26] surface treatment with air abrasion is a routinely followed laboratory procedure prior to porcelain addition.

The main drawback of most of these surface treatments is contamination of metal substrate, eventually decreasing the bond strength at the interface.[13,18] The application of lasers in dentistry has widened to include it as a means of altering the surface characteristics of metal veneering interface. Surface treatment with the neodymium yttrium aluminum garnet (Nd:YAG) laser is considered as an alternative to other surface treatment methods because of its depth of optical penetration depending on the material irradiated. Studies demonstrating Nd:YAG laser irradiation as a surface treatment modality of base metal alloys is sparse.[20]

In the literature, abundant information is available regarding bonding mechanism and the bond strength values of porcelain veneered to cast base metal alloys,[7,8,19,26,31] whereas studies regarding the same with porcelain veneered to laser sintered base metal alloys are few.[1,51] Further, dental interests in Co-Cr has also increased due to its low price and different fabrication methods available.

There are several tests capable of evaluating the veneering ceramic–metal core bond strength such as flexural mode, twist, shear, tension or combination of flexural and twist.[4] Many authors in the literature suggested the use of shear bond strength test as one of the most reliable methods to evaluate the bond strength because it concentrates the applied tension on the interface between two materials.[13] Failure mode of tested samples has been studied qualitatively using scanning electron microscope (SEM). Analysis of surface chemistry by energy dispersive x-ray microanalysis (EDX) to corroborate and quantify the SEM finding has also been reported.[2,5,20,51]

In the view of above considerations, the aim of the present in-vitro study was to evaluate and compare the shear bond strength of cast Co-Cr alloy and DMLS Co-Cr alloy to dental porcelain with the effect of sand blasting and laser etching surface treatments. Qualitative analysis was done using scanning electron microscope to determine the failure pattern of samples. Energy dispersive X-ray microanalysis (EDX) was used to evaluate the interface chemistry of the samples.

The objectives of the present study included the following:

1. To evaluate the shear bond strength between cast Co-Cr alloy and porcelain after surface treatment with sand blasting.
2. To evaluate the shear bond strength between cast Co-Cr alloy and porcelain after surface treatment with laser etching.
3. To evaluate the shear bond strength between DMLS Co-Cr alloy and porcelain after surface treatment with sand blasting.
4. To evaluate the shear bond strength between DMLS Co-Cr alloy and porcelain after surface treatment with laser etching.
5. To compare the shear bond strength values obtained from the four groups.
6. To compare the shear bond strength between cast Co-Cr alloy and porcelain after surface treatments with sand blasting and laser etching.
7. To compare the shear bond strength between cast and DMLS Co-Cr alloy and porcelain after surface treatment with sand blasting.
8. To compare the shear bond strength between cast Co-Cr alloy and porcelain after surface treatment with sand blasting and DMLS Co-Cr alloy and porcelain after surface treatment with laser etching.
9. To compare the shear bond strength between cast Co-Cr alloy and porcelain after surface treatment with laser etching and DMLS Co-Cr alloy and porcelain after surface treatment with sand blasting
10. To compare the shear bond strength between cast and DMLS Co-Cr alloy and porcelain after surface treatment with laser etching.

11. To compare the shear bond strength between DMLS Co-Cr alloy and porcelain after surface treatments with sand blasting and laser etching.
12. To evaluate qualitatively the mode of failure of the samples by Scanning Electron Microscopy (SEM analysis) and to evaluate the surface chemistry by Energy Dispersive X–ray microanalysis (EDX analysis).

REVIEW OF LITERATURE

Gilbert L. Jeremy et al (1994)[12] evaluated the effect of the bonding agent by comparing the shear bond strength and three- point bending strength of three combinations of materials (milled titanium/porcelain with bonding agent, milled titanium/porcelain without bonding agent and high palladium/porcelain). He concluded the use of a bonding agent improves the bond strength of porcelain fused to milled titanium.

White Shane N. et al (1996)[48] measured strength of layered porcelain fused to titanium beams, determined failure modes, and investigated the porcelain-titanium interface. The strength of layered porcelain-ceramic beams was limited by the tensile or compressive strengths of the porcelain, not by the interfacial bond. Scanning electron microscopy and energy-dispersive X-ray spectroscopy demonstrated that the bond was limited by delamination of a thin titanium-titanium oxide interface.

Lenz Jurgen et al (1998)[23] determined the residual thermal stresses in the specimen and calculated with the aid of the finite element method. The larger the Young's modulus of the alloy, the higher both stresses. The results permit a deeper comprehension of the debonding process in the test. Shear stress induced by loading increases the overall shear stress at the end of the bond interface, whereas load tensile stress is buffered by thermal compressive stress.

Graham Julia D. et al (1999)[13] compared the effect of seven different alloy surface treatments on the bond strength of the porcelain-metal interface. It was concluded that de-gassing the alloy prior to porcelain application increased the bond strength and excess surface grinding of the alloy reduced bond strength and steam cleaning the alloy surface prior to de-gassing and porcelain application also significantly reduced the bond strength.

Pecora Nikole et al (2002)[39] investigated to use two testing device Ultradent and unrestricted knife, to evaluate the shear bond strength of single-bottle adhesives with their multistep counterparts. They concluded that all bonding agents tested resulted in higher mean shear bond strengths when tested with the Ultradent testing device compared with the unrestricted knife.

Fischer J. (2002)[10] Investigated the metal–ceramic bonding and the effect of sand blasting on Au -Ti - Ir and Au–Pt–Pd based alloys. Concluded that Au – Ti-Ir is suitable for metal ceramic restorations and Chemical bond is much more important than mechanical interlocking produced by sand blasting. Larger grains of alumina do not significantly enhance the bond strength.

Liu Jie et al (2002)[25] examined the effect of degassing and sand blasting on the three-point flexure bond strength of low-fusing porcelain to cast titanium and compared the results with the strength of porcelain to gold alloy. Concluded that the bond strength between the two were comparable and it also depends on factors such as porcelain used and porcelain firing schedules (including degassing).

Bondioli R. Ilda et al (2004)[5] evaluated the shear bond strength of the interface of two dental porcelains, Triceram and Vita with pure titanium injected into a mold at three different temperatures of, 430^{o}C, 700^{o}C and 900^{o}C. They concluded that the Triceram porcelain bond strength decreased significantly with an increase in the casting temperature of pure titanium. The vita porcelain had the highest bond strength for a titanium mold casting temperature of 700^{0}C.

Murray K. Andrea et al (2005)[32] determined the effect of laser surface treatment of Ni–Cr alloy on tensile bond strength of a composite resin in comparison with a conventional sandblasting technique. Laser pre-treatment of Ni–Cr alloy increases bond strength to composite resin compared with sandblasting; laser pre-treatment in combination with sandblasting further increases de-bond strengths.

Hussaini Ibrahim Al et al (2005)[18] investigated effect of bonding agent and surface treatment using airborne-particle abrasion and hydrochloric acid on the bond strength between a low-fusing porcelain and commercially pure cast titanium. Surface treatment using either airborne-particle abrasion or bonding agent alone enhanced the bond strength of cast commercially pure titanium to low-fusing porcelain. Combination of airborne-particle abrasion and bonding agent provided the greatest improvement in titanium-ceramic bond strength. Hydrochloric acid surface treatment provided no beneficial effect to the titanium-ceramic bond strength.

De Melo Renata Marques et al (2005)[7] evaluated the shear bond strength between a porcelain system, IPS d.SIGN and four alternative alloys, two Ni-Cr alloys- 4 ALL and Wiron 99 and two Co-Cr alloys – IPS d.SIGN 20 and Argeloy NP. They concluded that the bond strength of the alloy, IPS d.SIGN 20, specifically developed for the ceramic system IPS d.SIGN was not different than the other three base metal alloys tested.

NETO Alfredo Julio FERNANDES et al (2006)[33] evaluated the metal/porcelain bond strength of three ceramic systems associated with three nickel-chromium alloys and one experimental cobalt-chromium-titanium alloy. Based on the results it was concluded that the bond strength of the three ceramic systems to the Ni-Cr and Co-Cr-Ti alloys varied significantly, indicating that metal/ceramic compatibility was very important to the bond strength.

Oyafusoa Denise Kanashiro et al (2008)[36] evaluated the effect of thermal and mechanical cycling alone or in combination, on the flexural strength of ceramic and metallic frameworks cast in gold alloy or titanium. The results showed the mean flexural strength values for the ceramic–gold alloy combination were significantly higher than those of the ceramic–cpTi combination regardless of the fatigue conditions performed. Mechanical and thermo-mechanical fatigue decreased the flexural strength results significantly for both ceramic–gold alloy and ceramic– cpTi combinations compared to the control group. Microscopic analysis of the specimen after flexural strength test showed complete adhesive detachment of the ceramic from cpTi framework exclusively indicating the weakest interface of the assembly was located between cpTi framework and its oxide layer.

Joias Renato Morales et al (2008)[19] evaluated the shear bond strength of a dental ceramic to 5 commercially available Co-Cr alloys. Five Co-Cr alloys (IPS d.SIGN 20, IPS d.SIGN 30, Remanium 2000, Heranium P and Wirobond C) were tested and compared to a control group of an Au-Pd alloy (Olympia). Mean bond strengths for IPS 20 and IPS 30 were not significantly different, but were significantly higher than mean bond strengths for the other 4 alloys, which were not significantly different from each other. Bond strength of a dental ceramic to a Co-Cr alloy is dependent on the alloy composition.

Akova Tolga et al (2008)[1] compared shear bond strengths of cast Ni-Cr and Co-Cr alloys and the laser sintered Co-Cr alloy to dental porcelain. They concluded their study saying that the new laser sintering technique for Co-Cr alloy appears promising for dental applications and it can be used as an alternative technique to conventional casting of dental alloys for porcelain fused to metal restorations.

Kim Jin-Tae et al (2009)[20] compared the effect of laser etching as a titanium surface treatment with 3 other surface treatments (machining, airborne-particle abrasion, and acid etching), evaluating their ability to enhance the bond strength between a titanium substrate and porcelain. Laser etching of titanium surfaces using an Nd/YAG laser was effective in improving bond strength with low-fusing porcelain, as compared to the acid-etching method. No significant difference between laser etching and airborne-particle-abrasion surface treatment.

Mehulić Ketij et al (2009)[31] investigated the influence of different cast surface finishing process (oxidation, sandblasting with 110 and 250 µm Al_2O_3, bonding agent, hydrochloric acid solution) on metal-ceramics bond strength.. The highest force for the separation of ceramics was found in samples sandblasted with 250µm Al_2O_3, oxidised and repeatedly sandblasted with 250 µm Al_2O_3, and the lowest force with the sample treated with hydrochloric acid solution. The oxidation, prolonged oxidation and the bonding agent do not influence the bond strength of the tested metal-ceramic system.

Aladag Akin et al (2010)[2] evaluated the effect of soldering and laser-welding procedures on the bond strength between ceramic and metal. Mean differences in µTBS of veneering ceramic to soldered and laser-welded metal surfaces were not significantly different and were significantly lower than that of cast alloy.

Galo Rodrigo et al (2010)[11] evaluated the bond strength of four dental ceramics (Triceram, Noritake Ti22, IPS and Noritake EX3) to commercially pure titanium. Shear bond strength means for the ceramics Triceram and Noritake Ti22 were higher than the minimum value required by the DIN 13927 standard. Ceramics IPS and Noritake EX3, although not specifically formulated for titanium, also had shear bond strength means above the ISO-recommended value. Ceramic Noritake Ti22 should be indicated for the commercially pure titanium casting due to its higher mean bond resistance compared to other ceramics utilized.

Lombardo Geraldo H. L. et al (2010)[26] evaluated influence of surface treatment on shear bond strength between a Co-Cr alloy and two ceramics. Ceramic and surface treatment significantly affected the mean bond strength values. Air-particle abrasion with Al_2O_3 improved shear bond strength between metal and ceramics used.

De Vasconcellos Luis Gustavo Oliveira et al (2010)[8] evaluated the effect of the opaque layer firing temperature and mechanical and thermal cycling on the flexural strength of a ceramic fused to commercial cobalt chromium alloy. Mechanical and thermal cycling did not significantly influence the flexural bond strength values for all opaque firing temperatures/ Co-Cr combinations tested when compared to control groups and opaque layer firing temperatures significantly increased the flexural bond strength values.

Kulunk Tolga et al (2011)[21] evaluated the effect of different air-abrasion particles on the shear bond strength of a ceramic to nickel-chromium (Ni-Cr) and cobalt-chromium (Co-Cr) alloys. The highest bond strengths were obtained in air abrasion with 110-µm Al_2O_3 particles and the lowest bond strengths were obtained with 50-µm Al_2O_3 particles. None of the other tested alternative air-abrasion particles provided superior bond strengths compared with 110-µm Al_2O_3 particles.

Lim Hyun-Pil et al (2011)[24] investigated the effect of various treatments on the fracture load of bonded titanium and porcelain components of crown restorations. The gold-coated titanium and TiN-coated titanium had significantly higher fracture loads than the airborne-particle-abraded titanium ceramic crowns. The gold-coated and TiN-coated titanium specimens demonstrated fracture loads similar to that of gold ceramic crowns. SEM/EDS showed that after the crowns fractured, the gold control group and gold- and TiN-coated titanium specimens had more adherent porcelain on their surfaces than the uncoated titanium that was airborne-particle abraded with Al_2O_3 particles.

Ortorp Anders et al (2011)[35] evaluated and compared the marginal and internal fit of three-unit FDPs made of Co–Cr using four fabrication techniques, and to conclude, in which area the largest misfit is present. Best fit based on the means for all measurement points was in the Direct metal laser sintering (DMLS) followed by Milled wax (MW) ,Lost wax(LW) and Milled Co-Cr (MC) groups. Significant differences were present between MC and DMLS.

Tara Milia Abou et al (2011)[44] evaluated the clinical outcome of posterior single-unit metal ceramic crowns fabricated using CAD- CAM laser-sintering technology. Sixty restorations were placed in 39 patients and cemented with glass-ionomer cement. Follow-ups were performed annually. During which one restoration was regarded a dropout, one failed (biologic failure), and one debonded. One abutment tooth had to be treated endodontically and three teeth were treated because of caries. No further technical complications, eg, veneering ceramic chipping, occurred during the observation period. The results suggest that the clinical outcome of posterior single-unit metal-ceramic crowns fabricated using laser-sintering technology is promising to that of conventionally fabricated metal ceramic crowns.

De Vasconcellos Luis Gustavo Oliveira (2011)[9] evaluated the effect of airborne-particle abrasion and mechanico-thermal cycling on the flexural strength of a ceramic fused to cobalt–chromium alloy or gold alloy. Sand blasting with Al_2O_3 at 10 and 20 mm improved the flexural bond strength between ceramics and alloys used and the mechanico-thermal cycling of metal-ceramic specimens resulted in a decrease of bond strength.

Xiang Nan et al (2012)[51] evaluated the metal–ceramic bond strength of a Co–Cr dental alloy prepared using a direct metal laser sintering (DMLS) technique. Fracture mode analysis and area fraction of adherence porcelain were determined by measuring Si content of specimens by SEM/EDS. No significant difference for the mean bond strength between the DMLS and traditional cast sample groups. The DMLS group showed significantly more porcelain adherence than the conventional cast Co-Cr.

MATERIALS AND METHODS

The present in-vitro study was conducted to evaluate and compare the shear bond strength of cast Co-Cr alloy and direct metal laser sintered (DMLS) Co-Cr alloy to dental porcelain with the effect of sand blasting and laser etching surface treatments.

The following materials, instruments and equipments were used for the preparation and testing of the cast and DMLS Co-Cr alloy-porcelain test samples:

MATERIALS EMPLOYED:

1. Poly vinyl siloxane (PVS) impression material, addition type, soft putty/ regular set (Aquasil, Dentsply, Germany) (Fig.1)
2. Inlay wax (GC Corporation, Tokyo, Japan) (Fig.2)
3. Sprue wax (Bego, Germany) (Fig.3)
4. PKT instruments (Delta Lab, Chennai, India) (Fig.4)
5. Silicon casting ring. (Delta labs, Arumbakkam, Chennai, India) (Fig.5)
6. Surfactant spray (Auro film, Bego, Germany) (Fig.6)
7. Phosphate bonded investment material (Bellasun, Bego, Germany) (Fig.7a)
8. Investment Liquid (Begosol, Bego, Germany) (Fig.7b)
9. Distilled water (Merck, Mumbai, India) (Fig.7c)

10. Cobalt-Chromium (Co-Cr) alloy pellets (Wirobond C, Bego, Germany) (Fig.8)
11. DMLS Co–Cr alloy powder (Sint-Tech, Clermont-Ferrand, France) (Fig.9)
12. Aluminum oxide powder 110µm (Delta labs, Chennai, India) (Fig.10a)
13. Aluminum oxide powder 250µm (Korox 250) (Fig.10b)
14. Carborundum separating discs (Dentorium, New York, USA) (Fig.11a)
15. Tungsten Carbide burs (Edenta, Switzerland) (Fig.11b)
16. Silicon Carbide rubber points (Dentsply, Germany) (Fig.11c)
17. Opaque porcelain (IPS dSIGN, Ivoclar, Vivadent, Liechtenstein) (Fig.12)
18. Leucite porcelain (IPS dSIGN, Ivoclar, Vivadent, Liechtenstein) (Fig.13)
19. Porcelain build-up liquid (IPS dSIGN, Ivoclar, Vivadent, Liechtenstein) (Fig.14)
20. Glaze (IPS dSIGN glazing paste, Ivoclar, Vivadent, Liechtenstein) (Fig.15)
21. Ceramic palette (Ivoclar, Vivadent, Liechtenstein) (Fig.16)
22. Ceramic holder (Ivoclar, Vivadent, Liechtenstein) (Fig.17)
23. Ceramic honey comb tray (Ivoclar, Vivadent, Liechtenstein) (Fig.18)
24. Ceramic brushes (Ivoclar, Vivadent, Liechtenstein) (Fig.19)
25. Tissue paper (Premier, India) (Fig.20)

INSTRUMENTS AND EQUIPMENTS EMPLOYED:

1. Vernier calliper (Aerospace, China) (Fig.21)
2. Vacuum power mixer (The continental, Whip Mix, Kentucky, USA) (Fig.22)
3. Burnout furnace (Technico, India) (Fig.23)
4. Induction casting machine (Fornax GEU, Bego, Germany) (Fig.24)
5. DMLS machine (PM 100, phenix systems, France) (Fig.25)
6. Alloy grinder (Whipmix, USA) (Fig.26)
7. Sand blaster (Ideal blaster, delta labs, Chennai) (Fig.27)
8. Nd:YAG laser welding machine (Lee laser, USA) (Fig.28)
9. Ultra sonic bath (Appa, Ultra Hygienic Equipments, India) (Fig.29)
10. Dental porcelain furnace (Vita Vacumat 40, Vita, Zahnfabric H, Badsackingen, Germany) (Fig.30)
11. Universal testing machine (Model LR 100K, Lloyd instruments, Farnharm, UK) (Fig.31)
12. Scanning Electron Microscope (Jeol, JSM-6390LA, USA) (Fig.32)

Description of the universal testing machine (Fig.28):

The universal testing machine (Model LR 100 K, Lloyd instruments, Farnham, UK) (Fig.31) was used to test for shear bond strength of the samples used in this study. This machine rests on a table top. It consists of a lower chamber, upper chamber, a display board to display the amount of force needed to fracture the veneering porcelain from metal substructure, and a computer.

The upper chamber is attached to the lower with the help of two horizontal bars, which also enclose the hydraulic pressure machine attached to upper member. The lower portion has a bench vice test specimen fixture to hold the test specimen. The upper portion has a lever grip on which a monobeveled chisel blade can be attached. The whole unit is attached to the computer for recording and converting data as required.

Description of the Scanning Electron Microscope (Fig.32):

Scanning electron microscope (Joel, JSM-6390LA) (Fig.32) use a beam of highly energetic electrons (1 KeV-1MeV) to examine objects on a very fine scale (0.2nm onwards). They can reveal the fine structure of variety of materials. As the name suggests, SEM uses a scanned beam rather a fixed beam. It is primarily used for the examination of thick specimens (i.e. electron opaque).The specimens to be magnified may have some conductivity and may get charged up. Hence they are coated with a platinum layer to prevent the charging up and in order to increase the secondary emissions. Sometimes the specimens may be coated with tungsten when higher magnifications are essential. The incident electron probe scans the sample surface and the signals produced are used to modulate the intensity of a synchronously scanned beam on a CRT screen. The electrons which are back scattered from the specimen are collected to provide (i) topographical information if low energy secondary electrons are collected (ii) atomic number and reorientation information if the higher energy, back scattered electrons are used. The magnification is given immediately by the ratio of the CRT scan size to be the specimen size.

The SEM was coupled with an energy-dispersive X-ray spectrometer (EDS) for elemental analysis of the metal-porcelain interface. EDX analysis was conducted on the bonding surface of both the Co-Cr alloy and porcelain test samples at 30x magnification.

METHODOLOGY:

I. Fabrication of cast and DMLS Co-Cr alloy specimens

A. Preparation of cast Co-Cr alloy specimens:

1. Fabrication of custom-milled master die
2. Obtaining putty index of master die
3. Preparation of wax patterns
4. Spruing of wax patterns
5. Investment of wax patterns
6. Burn out procedure
7. Casting procedure
8. Divesting and Finishing

B. Preparation of DMLS Co-Cr alloy specimens:

1. Designing the samples using Auto CAD in STL file format
2. Fabrication of samples in the laser sintering unit

II. Surface treatments of cast and DMLS Co-Cr alloy specimens

A. Surface treatment with Sand blasting

B. Surface treatment with Laser etching

III. Veneering of cast and DMLS Co-Cr alloy specimens with porcelain

A. Opaque layer application

B. Application of body ceramic

C. Glazing of samples

IV. Grouping of test samples

V. Testing of test samples for shear bond strength

VI. Statistical analysis

VII. SEM and EDX analysis

I. Fabrication of cast and DMLS Co-Cr alloy specimens

A. Preparation of cast Co-Cr alloy specimens (Fig.33-49)

1. Fabrication of custom-milled master die (Fig.33)

In the present study, four custom-milled, stainless steel, cylindrical master dies of 4mm x 4mm dimensions and a base of 5mm x 1 mm dimension were fabricated to obtain Co-Cr alloy specimens of standardized dimensions.

2. Obtaining putty index of master die (Fig.34)

A putty index was obtained to facilitate standardisation of wax pattern dimensions. Addition polymerising poly vinyl silaxane, putty material (Aquasil, Dentsply, Germany) (Fig.1) was mixed as per the manufacturer’s instructions and the four master dies were impressed into it and held firmly until the material set. Upon setting the master dies were removed to reveal four mold spaces.

3. Preparation of Wax patterns (Fig.35)

Inlay casting wax (GC Corporation, Japan) was melted and poured into the mold spaces to obtain twenty cylindrical blocks of size 4 mm length x 4mm diameter with base of 1mm height and 5mm diameter. Each wax pattern dimension was checked for accuracy using a vernier calliper (Aerospace, China) (Fig.36)

4. Spruing of wax patterns (Fig.37)

Sprue wax (Bego, Germany) of 2.5mm diameter and 30mm length were attached to the patterns. The other ends of the sprues were attached to the crucible former. The wax patterns were sprayed with wax surfactant spray (Aurofilm, Bego, Germany) to improve wettability of wax pattern.

5. Investment of wax patterns (Fig.38-41)

Suitable size of silicon casting ring (Delta, Chennai) was selected and positioned on the crucible former around the prepared wax pattern (Fig.38). The phosphate bonded investment material (Bellasun, Bego, Germany) was mixed with the investment liquid (Begosol, Bego, Germany) in a vacuum mixer machine (The continental, Whipmix, USA) (Fig.22, 39) and the prepared wax patterns were invested (Fig.34). Since the ringless casting procedure was adapted in the study, the silicon ring was removed after the investment material had set (Fig.41).

6. Burn-out procedure (Fig.42)

The set investment mold was placed in the burnout furnace (Technico, India) (Fig.42) at room temperature. Investment mold was allowed to heat continuously till 950^0 C at the rate of 8^0C /min and was held for 30 mins at 950^0C.

7. Casting Procedure (Fig.43, 44)

Casting procedure was performed quickly to prevent heat loss from the mold. After burnout, investment mold was taken out of the furnace and was placed in the casting machine (Fig.24). Casting was done in an induction casting machine (Fornax GEU, Bego, Germany) (Fig.24). The Chrome–Cobalt alloy (Bego, Germany) was heated sufficiently till the alloy ingot turned into molten state and the crucible was released and the centrifugal force ensured completion of casting procedure. Investment with cast was allowed to cool down to room temperature (Fig.44).

8. Divesting and Finishing (Fig.45-49)

The retrieved casting were divested using 110µm alumina and casting was retrieved. Sprues were cut with the carborundum separating discs (Fig.47). The same procedure was carried out for all twenty samples. Tungsten carbide trimmers were used to reduce the sprue-attached area of the base metal alloy substructure. Finishing of base metal alloy substructure was done with silicon carbide rubber points. Thus 20 cast Co-Cr alloy specimens were fabricated (Fig.49) and divided into two groups (Gr I & Gr II) with 10 specimens (n=10) for each group and subjected to two types of surface treatments.

B. Preparation of DMLS Co – Cr alloy specimens

1. Designing the samples using Auto CAD in STL file format

As the custom-milled master die had parallel walls resulting in less than optimum scan data using an optical scanner, the alloy samples for DMLS technique were designed using AUTOCAD software to match the dimensions of the master die. This was stored in STL file format, which was fed to the CAM Bridge (It is a professional software for automated part placement, orientation and identification, if in case multiple scanned STL data are fed to the CAM Bridge).

2. Fabrication of samples in the laser sintering unit (Fig.50)

From the CAM Bridge the data was forwarded to the building chamber, where infrared laser beam was used to fuse the (Co-Cr) powder, layer by layer to produce the solid object. Production began once a layer of powder is spread across the build platform, which then was evenly spread with a powder leveling roller. The laser beam scans the powder surface, heats the particles and fuses them. After the first layer solidifies the build platform moves another layer of powder, which is again sintered by the laser beam. The process is repeated until the sample is completed. Thus 20 DMLS Co-Cr alloy specimens were fabricated (Fig.50) and divided into two groups (Gr III & Gr IV) with 10 specimens (n=10) for each group and subjected to two types surface treatments.

II. Surface treatments of cast and DMLS Co-Cr alloy specimens

A. Surface treatment with Sand blasting (Fig.51, 52)

The surface of the cast (Group I, n=10) and DMLS (Group III, n=10) Co-Cr alloy specimens (4 mm Diameter Circular area) which had to be veneered with porcelain was subjected to sand blasting with 250μ Al_2O_3 particles (Korox, Bego, Germany) (Fig.51) at 3-4 bar pressure and the surface treated samples (Fig.29) were immersed in ultrasonic bath with Isopropyl alcohol for 3 minutes prior to addition of Leucite porcelain (IPS dSIGN, Ivoclar Vivadent, Germany).

B. Surface treatment with Laser etching (Fig.53, 54)

A commercial based Nd:YAG laser (Q- switched, Lee laser, USA) with wavelength of 1064nm at 4 kHz was used to treat the surface of the cast and DMLS Co-Cr alloy specimens. The ablation of the surface was done at the power setting of 2kW with working duration of 32 seconds with the cutting speed of 100mm per second. Pulse energies were standardized to give an output fluence of 4.9J/cm.[2]

The surface of the 10 cast (Group II) (n=10) and 10 DMLS (Group IV) (n=10) Co-Cr alloy specimens (4 mm diameter circular area) which had to be veneered with porcelain was laser etched (Fig.53) and the laser etched samples (Fig.54) were immersed in ultrasonic bath (Fig.29) in Isopropyl alcohol for 3 minutes prior to addition Leucite porcelain. (IPS dSIGN, Ivoclar Vivadent, Germany)

III. Veneering of cast and DMLS Co-Cr alloy specimens with porcelain (Fig.55a, 55b)

All the specimens of Groups I-IV were veneered with porcelain in a similar manner as described below:

a. Opaque layer application

One opaque layer of ceramic was applied to the Co-Cr alloy specimen, condensed and fired to the metal surface to form a layer of 0.5 mm height, following that a second opaque layer was condensed and fired on the initial opaque layer to obtain a 1 mm thick opaque layer for each specimen. A2 shade was used to veneer the Co-Cr alloy specimen. The porcelain firing procedure was done in a dental porcelain furnace following the manufacturer's recommendations as mentioned below:

PROCEDURE	T (°C)	B (°C)	S (min)	t↗ (°C)	H (min)	V1 (°C)	V2 (°C)
I Opaque	900	403	6	80	1	450	889
II Opaque	890	403	6	80	1	450	889
I Body	870	403	4-9	60	1	450	869
II Body	870	403	4-9	60	1	450	869
Glaze	830	403	4	60	0.5-1in	450	829

b. Application of body porcelain.

Dentin porcelain of same shade (IPS dSIGN, Ivoclar, Vivadent, Liechtenstein.) (Fig.55b) was condensed on to the opaque ceramic at a height of

3 mm to reach a total ceramic height of 4mm, subsequently firing procedure was done according to the instructions of the manufacturer. After cooling metal ceramic specimens were finished with a medium grit laboratory bur.

c. Glazing of samples:

Glazing of the samples was done using Glaze (IPS dSIGN glazing paste, Ivoclar, Vivadent, Liechtenstein).

IV. Grouping of test samples (Fig.56-59)

A total of 40 Co-Cr alloy – porcelain test samples were prepared and assigned to four experimental groups:

Group I (n=10) cast Co-Cr alloy-porcelain test samples after surface treatment with sand blasting (Fig.56)

Group II (n=10) cast Co-Cr alloy-porcelain test samples after surface treatment with laser etching (Fig.57)

Group III (n=10) DMLS Co-Cr alloy-porcelain test samples with surface treatment with sand blasting (Fig.58)

Group IV (n=10) DMLS Co-Cr alloy-porcelain test samples after surface treatment with laser etching (Fig.59)

V. Testing of test samples for shear bond strength

a. Mounting of samples (Fig.60, 61):

Each test sample was individually fixed in the jig of dimensions of 37 mm x 39mm x 41mm with screws (Fig.60, 61). The level of the core veneer interface of the test samples was positioned to enable the evaluation of shear bond strength with the universal testing machine (Model LR 100K, Lloyd instruments, Farnharm, UK) (Fig.31). In this manner all forty test samples were mounted for the evaluation of shear bond strength.

b. Testing of samples (Fig.62, 63)

A total of forty test samples (Group I, II, III and IV) were tested for shear bond strength in universal testing machine (Model LR 100K, Lloyd instruments, Farnharm, UK) (Fig.31, 62, 63). Each test sample was fixed to the sample fixture at the bench vice of the machine with the monobeveled chisel blade placed adjacent to and directly to the bonding interface. Force was applied to the sample so that the shear load was exerted adjacent to and directly to the bonding interface at a cross head speed of 0.5 mm / min until fracture occurred. Load deflection curves and ultimate load to failure were recorded automatically and displayed by the computer software of the testing machine. Shear bond force value at failure was recorded in Newtons, and shear bond strength (Mpa) was calculated by dividing the maximum load at which failure occurred by the bonding surface area

Shearbond strength (MPa) = Load (N) ÷ surface area (mm^2)

The basic values of shear bond strength of all the samples in four groups were tabulated. The mean shear bond strength for each group was calculated and tabulated for statistical analysis.

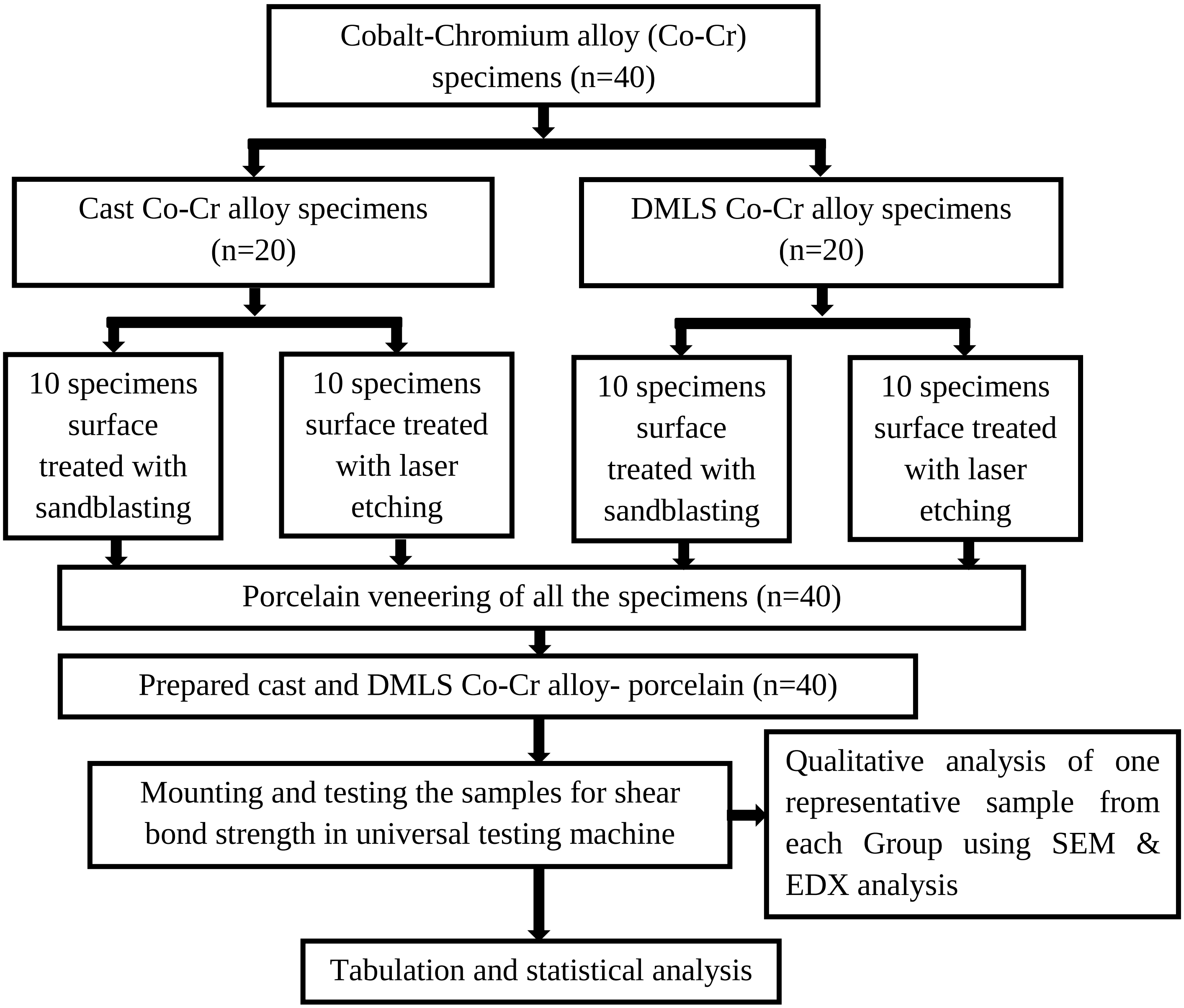
VI. Statistical Analysis:

The data was analyzed using the software SPSS -16. Descriptive statistics was used to find the mean and standard deviation of variables using one-way ANOVA. Post-hoc Tukey HSD test was used for multiple comparisons of the bond strength within the groups. P value <0.05 was considered as the level of significance.

VII. SEM and EDX analysis:

To determine the mode of failure, one fractured sample from each test group was randomly selected and examined under scanning electron microscope (Jeol, JSM-6390LA) (Fig.32) under 30x and 1000x magnifications. Surface chemistry was analyzed using energy dispersive X–ray microanalysis under 30x magnification (EDX analysis). The failure modes were presented along with results.

METHODOLOGY- OVERVIEW



Group I - Cast Co-Cr alloy-porcelain test samples after surface treatment with sandblasting.

Group II - Cast Co-Cr alloy-porcelain test samples after surface treatment with laser etching.

Group III - DMLS Co-Cr alloy-porcelain test samples after surface treatment with sandblasting.

Group IV - DMLS Co-Cr alloy-porcelain test samples after surface treatment with laser etching.

MATERIALS

Fig.1: Poly vinyl siloxane (PVS) Soft putty

Fig.2: Inlay wax

Fig.3: Sprue wax

Fig.4: PKT Instruments

Fig.5: Silicone casting ring

Fig.6: Surfactant spray

Fig.7a: Phosphate bonded Investment material

Fig.7b: Investment liquid

Fig.7c: Distilled water

Fig.8: Co-Cr alloy pellets

Fig.9: DMLS Co-Cr alloy powder

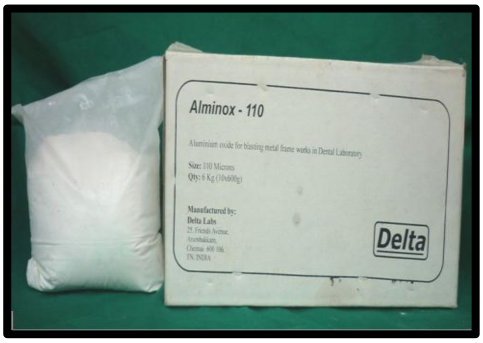


Fig.10a: Aluminum oxide powder 110µm

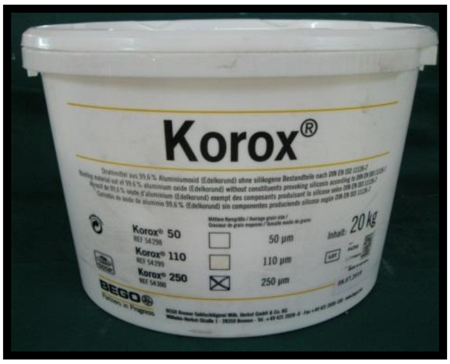


Fig.10b: Aluminum oxide powder 250µm

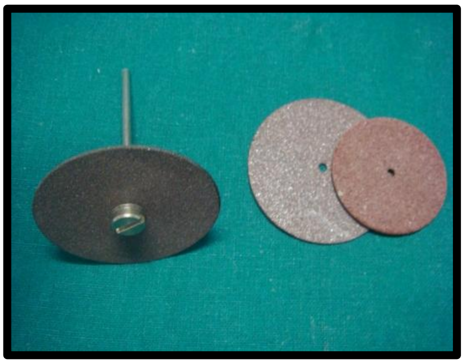


Fig.11a: Carborundum separating discs

Fig.11b: Tungsten carbide burs

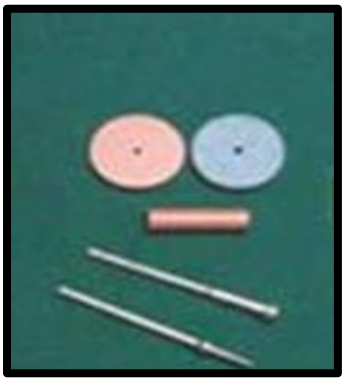


Fig.11c: Silicon carbide rubber points

Fig.12: Opaque porcelain

Fig.13: Leucite porcelain

Fig.14: Build-up liquid

Fig.15: Glaze paste

Fig.16: Ceramic palette

Fig.17: Ceramic holder

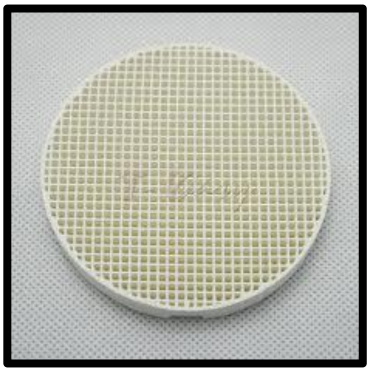


Fig.18: Ceramic honey comb tray

Fig.19: Ceramic brushes

Fig.20: Tissue paper

INSTRUMENTS AND EQUIPMENTS

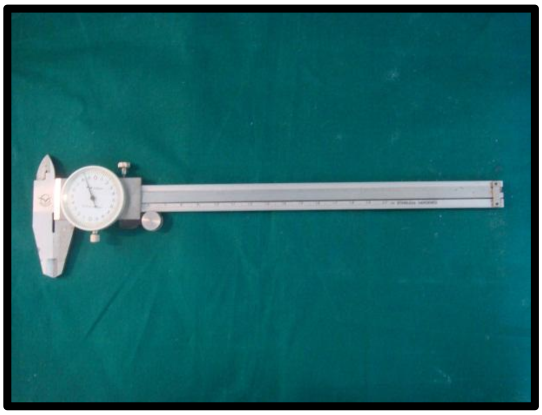


Fig.21: Vernier Calliper

Fig.22: Vacuum power mixer

Fig.23: Burnout furnace

Fig.24: Induction casting machine

Fig.25: DMLS machine

Fig.26: Alloy grinder

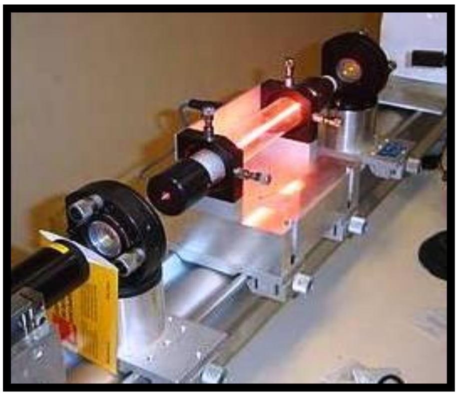


Fig.27: Sand blaster

Fig.28: Nd:YAG laser machine

Fig.29: Ultra sonic bath

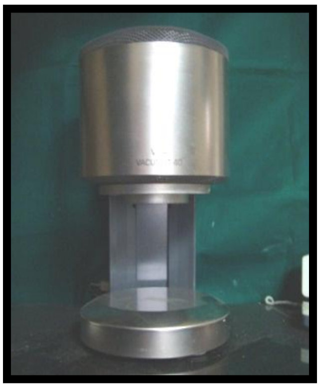


Fig.30: Dental porcelain furnace

Fig.31: Universal testing machine

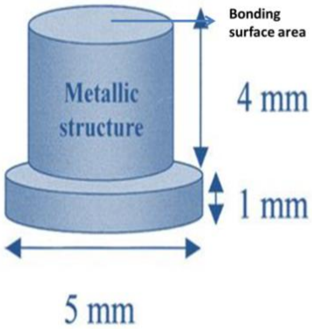
Fig.32: Scanning Electron Microscope

METHODOLOGY

I. FABRICATION OF CAST AND DMLS Co-Cr ALLOY-PORCELAIN SPECIMENS

A. PREPARATION OF CAST Co-Cr ALLOY SUBSTRUCTURE

a



b

Fig.33a: Custom milled master die

Fig.33b: Schematic representation of custom milled master die

Fig.34: Putty index of master die

Fig.35: Preparation of wax pattern

Fig.36: Checking dimensions of wax pattern

Fig.37: Spruing of wax patterns

Fig.38: Wax pattern inside the Siliring

Fig.39: Vacuum mixing the investment

Fig.40: Investing the wax pattern

Fig.41: Wax pattern inside the set refractory mold

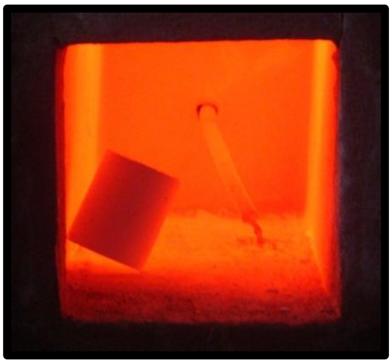


Fig.42: Burn-out Procedure

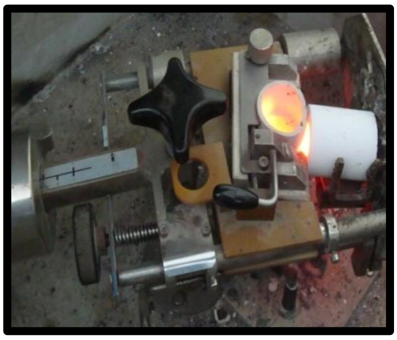


Fig.43: Casting Procedure

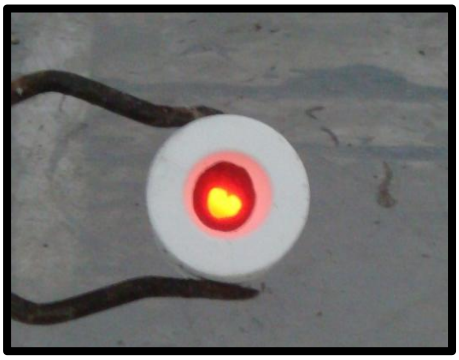


Fig.44: Refractory mould after casting

Fig.45: Retrieval of casting

Fig.46: Divested samples

Fig.47: Cutting of the sprues

Fig.48: Trimming and finishing

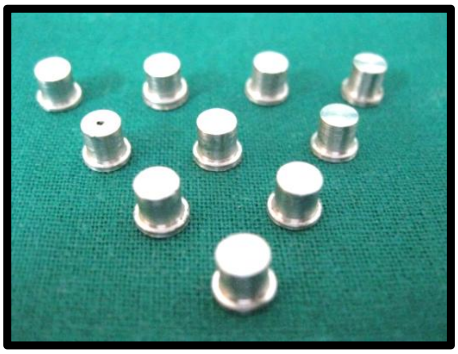


Fig.49: Cast Co-Cr samples

B. PREPARATION OF LASER SINTERED Co – Cr ALLOY SPECIMENS:

Fig.50: DMLS samples

II. SURFACE TREATMENT OF CAST AND DMLS Co-Cr ALLOY SPECIMENS

SAND BLASTING

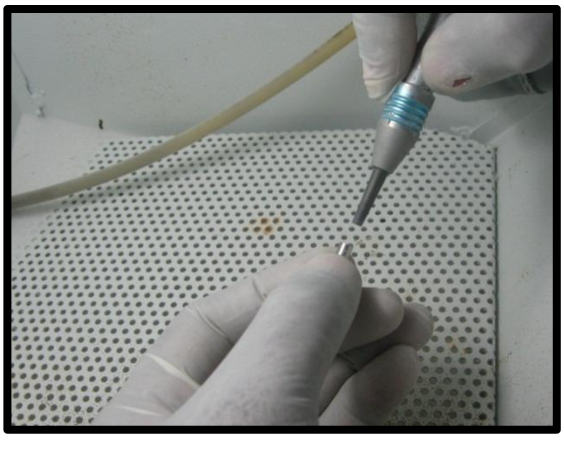
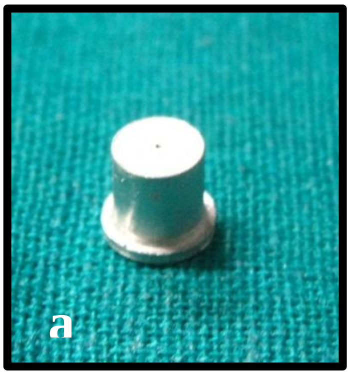


Fig.51: Surface treatment with 250µm Alumina



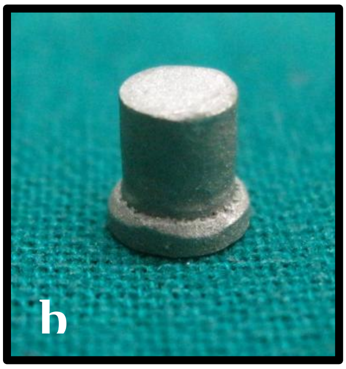


Fig.52a: Sandblasted cast Co-Cr sample

Fig.52b: Sandblasted DMLS Co-Cr sample

LASER ETCHING

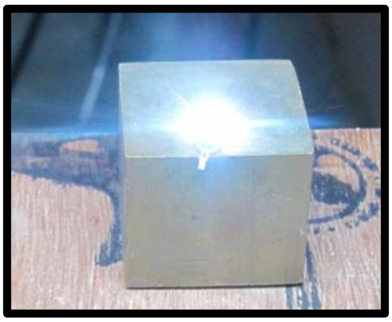


Fig.53: Laser etching of sample

Fig.54: Nd:YAG laser etched sample

III. VENEERING OF Co-Cr ALLOY SUBSTRUCTURES WITH PORCELAIN

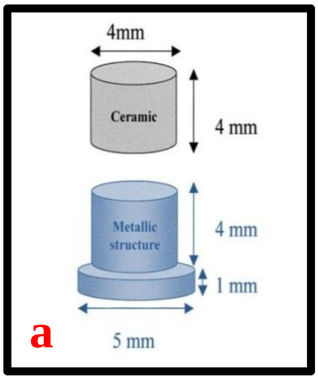


Fig.55a: Schematic representation of Co-Cr alloy ceramic test sample

Fig.55b: Porcelain veneering of Co-Cr sample

IV. GROUPING OF THE TEST SAMPLES

Fig.56: Porcelain veneered to cast Co–Cr alloy after sand blasting (Group I)

Fig.57: Porcelain veneered to cast Co–Cr alloy after laser etching (Group II)

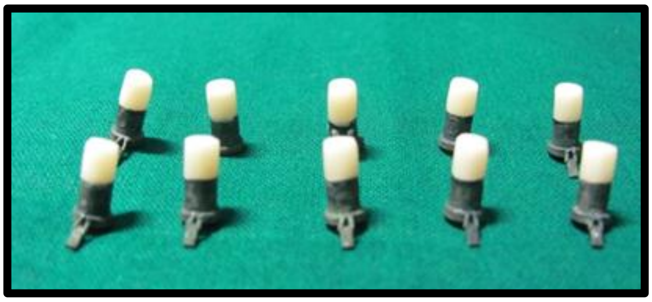


Fig.58: Porcelain veneered to DMLS Co-Cr alloy after sandblasting (Group III)

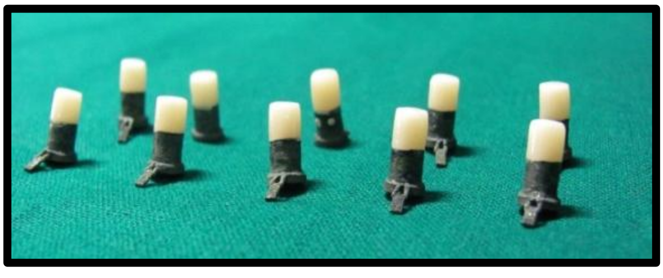


Fig.59: Porcelain veneered to DMLS Co-Cr alloy after laser etching (Group IV)

V. TESTING OF TEST SAMPLES FOR SHEAR BOND STRENGTH

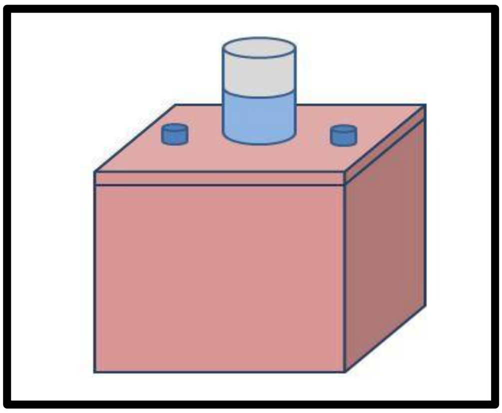


Fig.60: Schematic representation of test sample embedded in the jig

Fig.61: Test Sample fixed to the jig

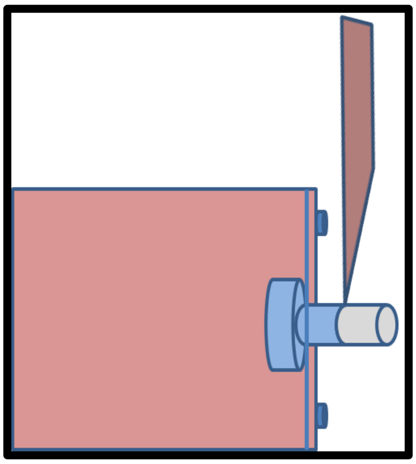


Fig.62: Schematic representation of shear bond strength testing of sample

Fig.63: Sample testing in universal testing machine

Fig.64 Debonded cast Co–Cr alloy-porcelain test samples after sandblasting

Fig.65: Debonded cast Co–Cr alloy-porcelain test samples after laser etching

Fig.66: Debonded DMLS Co-Cr alloy-porcelain test samples after sandblasting

Fig.67: Debonded DMLS Co-Cr alloy-porcelain test samples after laser etching

RESULTS

The present in vitro study was conducted for the comparative evaluation of shear bond strength of cast Co-Cr alloy and the direct metal laser sintering (DMLS) Co-Cr alloy to dental porcelain with the effect of sand blasting and laser etching surface treatments.

A total of forty samples were prepared and randomly divided into four test groups of ten samples each (Group I, II, III, and IV). Twenty cast Co-Cr alloy- porcelain samples were prepared and divided into two groups (Group I and Group II) for sand blasting and laser etching surface treatments. The Group I (n=10) cast Co-Cr alloy-porcelain test samples after surface treatment with sand blasting. The group II (n=10) cast Co-Cr alloy-porcelain test samples after surface treatment with laser etching. Twenty DMLS Co-Cr alloy-porcelain samples were prepared and divided into two groups (Group III and Group IV) for sand blasting and laser etching. The group III (n=10) DMLS Co-Cr alloy-porcelain test samples after surface treatment with sand blasting. The Group IV (n=10) DMLS Co-Cr alloy-porcelain test samples after surface treatment with laser etching. All samples were tested for shear bond strength in universal testing machine. The basic values of shear bond strength of all test samples in four groups were tabulated. The results were subjected for statistical analysis. One test sample from each group were randomly selected and subjected to qualitative analysis using scanning electron microscope (SEM) and energy dispersive spectrometer (EDS).

Table 1 shows the basic values of shear bond strength between cast Co-Cr alloy and porcelain test samples after surface treatment with sand blasting (Group I)

Table 2 shows the basic values of shear bond strength between cast Co-Cr alloy and porcelain test samples after surface treatment with laser etching (Group II)

Table 3 shows the basic values of shear bond strength between DMLS Co-Cr alloy and porcelain test samples after surface treatment with sand blasting (Group III)

Table 4 shows the basic values of shear bond strength between DMLS Co-Cr alloy and porcelain test samples after surface treatment with laser etching (Group IV)

Table 5 shows the mean shear bond strength obtained from basic values of four Groups (Group I, II, III & IV)

Table 6 shows the comparison of mean and standard deviation of shear bond strength between groups I, II, III and IV using One-Way Analysis of Variance (ANOVA)

Table 7 shows multiple comparisons of mean and standard deviation of shear bond strength within Groups using Post-hoc Tukey HSD analysis

Table 8 shows the comparison of mean shear bond strength of cast Co-Cr alloy-porcelain test samples after surface treatments with sandblasting (Group I) and laser etching (Group II) using Post-hoc Tukey HSD Analysis.

Table 9 shows the comparison of mean shear bond strength between cast Co-Cr alloy-porcelain (Group I) and DMLS Co-Cr alloy-porcelain (Group III) test samples after surface treatment with sandblasting using Post-hoc Tukey HSD Analysis.

Table 10 shows the comparison of mean shear bond strength between cast Co-Cr alloy-porcelain after surface treatment with sandblasting (Group I) and DMLS Co-Cr alloy-porcelain after surface treatment with laser etching (Group IV) using Post-hoc Tukey HSD Analysis.

Table 11 shows the comparison of mean shear bond strength between cast Co-Cr alloy-porcelain after surface treatment with laser etching (Group II) and DMLS Co-Cr alloy-porcelain after surface treatment with sandblasting (Group III) using Post-hoc Tukey HSD Analysis

Table 12 shows the comparison of mean shear bond strength between cast Co-Cr alloy-porcelain (Group II) and DMLS Co-Cr alloy-porcelain (Group IV) after surface treatment with laser etching using Post-hoc Tukey HSD Analysis)

Table 13 shows the comparison of mean shear bond strength of DMLS Co-Cr alloy-porcelain after surface treatment with sandblasting (Group III) and laser etching (Group IV) using Post-hoc Tukey HSD Analysis

Table 1 – Basic values of shear bond strength between cast Co-Cr alloy and porcelain test samples after surface treatment with sand blasting (Group I)

Samples	**Shear bond strength (MPa)**
1	67.54
2	69.14
3	72.04
4	66.14
5	74.64
6	67.64
7	70.64
8	70.94
9	70.04
10	73.34
Mean value	**70.21**

The highest shear bond strength of cast Co-Cr alloy and porcelain test sample after sand blasting was 74.64 MPa and the lowest was 66.14 MPa. The mean shear bond strength was found to be 70.21 MPa.

Table 2 – Basic values of shear bond strength between cast Co-Cr alloy and porcelain test samples after surface treatment with laser etching (Group II)

Samples	Shear bond strength (MPa)
1	73.03
2	71.53
3	72.97
4	71.04
5	72.05
6	71.02
7	72.47
8	73.83
9	72.67
10	72.04
Mean value	**72.26**

The highest shear bond strength of cast Co-Cr alloy and porcelain test sample after laser etching was 73.83 MPa and the lowest was 71.02 MPa. The mean shear bond strength was found to be 72.26 MPa.

Table 3 - Basic values of shear bond strength between DMLS Co-Cr alloy and porcelain test samples after surface treatment with sand blasting (Group III)

Samples	**Shear bond strength (MPa)**
1	69.94
2	66.64
3	71.24
4	72.31
5	70.44
6	71.54
7	72.22
8	73.64
9	69.64
10	72.24
Mean value	**71.00**

The highest shear bond strength of DMLS Co-Cr alloy and porcelain test sample after sandblasting was 73.64 MPa and the lowest was 66.64 MPa. The mean shear bond strength was found to be 71.00 MPa.

Table 4 - Basic values of shear bond strength between DMLS Co-Cr alloy and porcelain test samples after surface treatment with laser etching (Group IV)

Samples	Shear bond strength (MPa)
1	73.83
2	72.34
3	71.09
4	72.62
5	71.93
6	73.33
7	71.56
8	72.75
9	72.98
10	71.36
Mean value	**72.37**

The highest shear bond strength of DMLS Co-Cr alloy and porcelain test sample after laser etching was 73.83 MPa and the lowest was 71.09 MPa. The mean shear bond strength was found to be 72.37 MPa.

Table 5 – Mean shear bond strength obtained from basic values of four Groups (Group I, II, III & IV)

	Group I	Group II	Group III	Group IV
Mean (MPa)	70.21	72.26	71.00	72.37

Table 5 shows the mean shear bond strength between cast Co-Cr alloy-ceramic and DMLS Co-Cr alloy-ceramic samples surface treated with sand blasting and laser etching of four groups (Group I, Group II, Group III, and Group IV).

STATISTICAL ANALYSIS

The data was analyzed using the software SPSS-16. Mean and standard deviations were estimated from the samples of each test group. Descriptive statistics was used to find the mean and standard deviation variables. Post hoc test was used to compare the bond strength between groups. $P< 0.05$ was considered as the level of significance.

Table 6 - Comparison of mean and standard deviation of shear bond strength between Groups I,II ,III and IV using One-Way Analysis of variance (ANOVA)

GROUP	MEAN	SD	P - Value
GROUP I	**70.21***	**2.69**	0.027*
GROUP II	**72.27***	**0.91**	
GROUP III	**71.01***	**1.97**	
GROUP IV	**72.38***	**0.89**	

*-Mean difference is significant at 5% level

Inference: The one way Anova analysis was done to compare the groups and when analysed, there was a significant difference among the groups (P value = 0.027). As the one way Anova analysis shows the significant results, significance between the sub groups was analysed using post hoc -Tukey HSD.

Group IV > Group II > Group III > Group I

Table 7 - Multiple comparisons of the mean and standard deviation of shear bond strength within Groups using Post-hoc Tukey HSD analysis

(I) Group	(J) Group	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
Group I	Group II	-2.0550	.79746	.065	-4.2027	.0927
	Group III	-.7970	.79746	.751	-2.9447	1.3507
	Group IV	-2.1690	.79746	.047*	-4.3167	-.0213
Group II	Group I	2.0550	.79746	.065	-.0927	4.2027
	Group III	1.2580	.79746	.404	-.8897	3.4057
	Group IV	-.1140	.79746	.999	-2.2617	2.0337
Group III	Group I	.7970	.79746	.751	-1.3507	2.9447
	Group II	-1.2580	.79746	.404	-3.4057	.8897
	Group IV	-1.3720	.79746	.328	-3.5197	.7757
Group IV	Group I	2.1690	.79746	.047*	.0213	4.3167
	Group II	.1140	.79746	.999	-2.0337	2.2617
	Group III	1.3720	.79746	.328	-.7757	3.5197

*- Mean difference is significant at 5 % level

The post Tukey HSD analysis was done to compare with in the groups. The analysis have shown that there is no statistically significant difference between the groups studied except Group I and Group IV, which showed statistical significance.

The post-hoc Tukey comparisons are tabulated individually for each test group as under:

Table 8– Comparison of mean shear bond strength of cast Co-Cr alloy–porcelain test samples after surface treatments with sandblasting (Group I) and laser etching (Group II) using Post-hoc Tukey HSD Analysis

Groups	No. of samples	Mean	SD	P- value
Group I	10	70.21	2.68661	0.065
Group II	10	72.26	0.90831	

*-Mean difference is significant at 5% level

Inference: The mean shear bond strength of Group II is higher than that of Group I but the increase in mean value is statistically insignificant.

Table 9 - Comparison of mean shear bond strength between cast Co-Cr alloy-porcelain (Group I) and DMLS Co-Cr alloy-porcelain (Group III) test samples after surface treatment with sandblasting using Post-hoc Tukey HSD Analysis

Groups	No. of samples	Mean	SD	P -value
Group I	10	70.21	2.68661	0.79746
Group III	10	71.00	1.97039	

*-Mean difference is significant at 5% level

Inference: The mean shear bond strength of Group III is higher than that of Group I but the increase in mean value is statistically insignificant

Table 10- Comparison of mean shear bond strength between cast Co-Cr alloy -porcelain after surface treatment with sandblasting (Group I) and DMLS Co-Cr alloy - porcelain after surface treatment with laser etching (Group IV) using Post-hoc Tukey HSD Analysis

Groups	No. of samples	Mean	SD	P - value
Group I	10	70.21	2.69	0.047*
Group IV	10	71.00	.89	

*- Mean difference is significant at 5 % level

Inference: The mean shear bond strength value of Group IV is higher than Group I and the increase in the mean value is statistically significant with P-value (0.047).

Table 11- Comparison of mean shear bond strength between cast Co-Cr alloy -porcelain after surface treatment with laser etching (Group II) and DMLS Co-Cr alloy -porcelain after surface treatment with sandblasting (Group III) using Post-hoc Tukey HSD Analysis

Groups	No. of samples	Mean	SD	P- value
Group II	10	72.27	0.91	0.404
Group III	10	71.01	1.97	

*-Mean difference is significant at 5% level

Inference: The mean shear bond strength of Group II is higher than that of Group III but the increase in mean value is statistically insignificant.

Table 12- Comparison of mean shear bond strength between cast Co-Cr alloy-porcelain (Group II) and DMLS Co-Cr alloy-porcelain (Group IV) after surface treatment with laser etching using Post-hoc Tukey HSD Analysis

Groups	No. of samples	Mean	SD	P- value
Group II	10	72.26	0.90831	0.999
Group IV	10	72.37	0.89072	

*- Mean difference is significant at 5 % level

Inference: The mean shear bond strength of Group IV is higher than that of Group II but the increase in mean value is statistically insignificant.

Table 13- Comparison of mean shear bond strength of DMLS Co-Cr alloy-porcelain after surface treatment with sandblasting (Group III) and laser etching (Group IV) using Post-hoc Tukey HSD Analysis

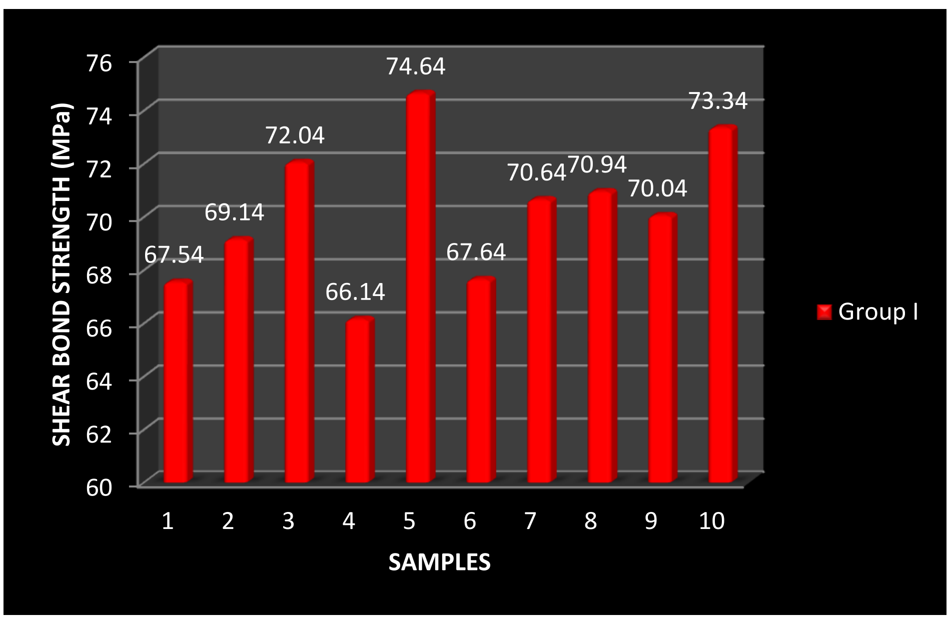
Groups	No. of samples	Mean	SD	P- value
Group III	10	71.00	1.97039	0.328
Group IV	10	72.37	0.89072	

*- Mean difference is significant at 5 % level

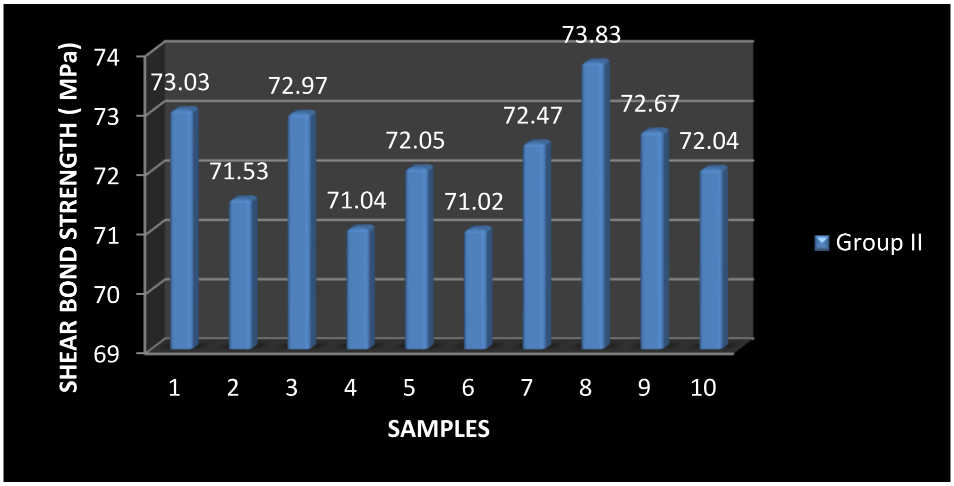
Inference: The mean shear bond strength of Group IV is higher than that of Group III but the increase in mean value is statistically insignificant.

Graph 1, 2, 3 and **4** shows the basic data of the results obtained in the study for the shear bond strength of samples in Group I, Group II, Group III and Group IV respectively. Graph V shows comparison of mean shear bond strength obtained from basic values of four groups.

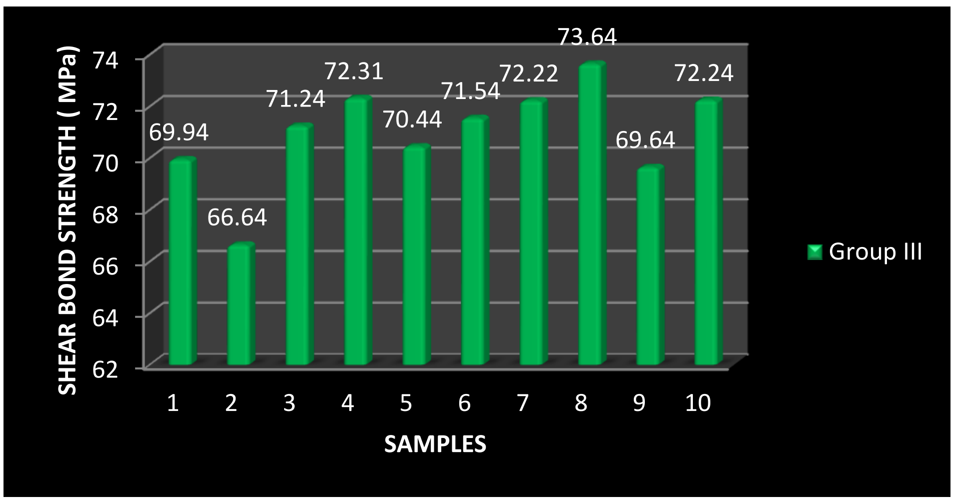
Graph 1: Basic values of mean shear bond strength of cast Co-Cr alloy-porcelain samples after sand blasting (Group I)



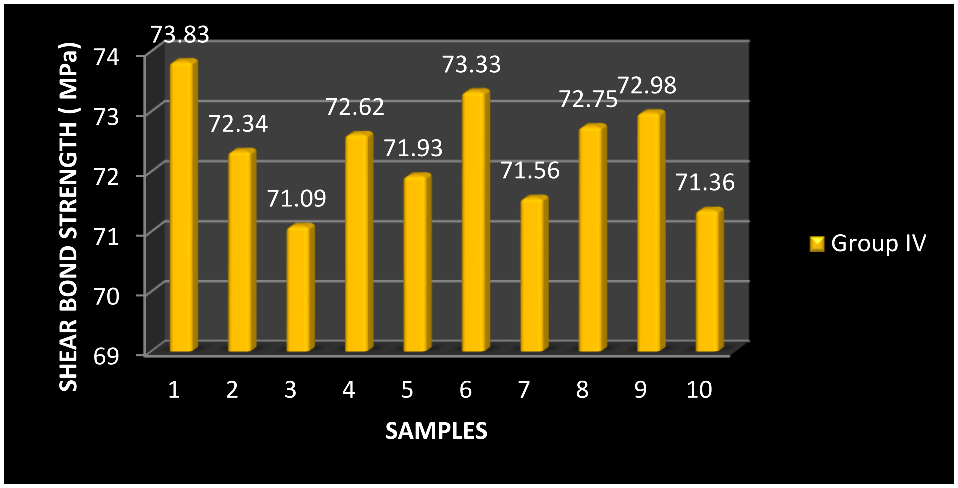
Graph 2: Basic values of mean shear bond strength of cast Co-Cr alloy- porcelain samples after laser etching (Group II)



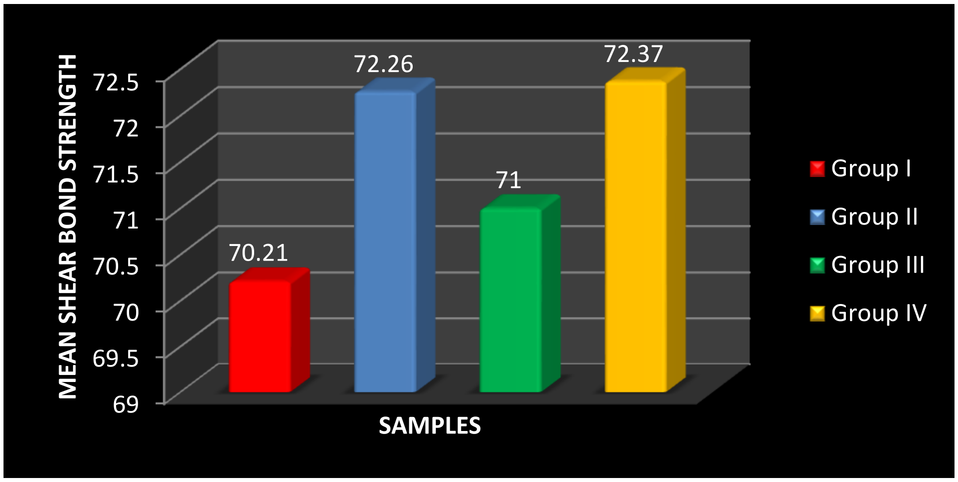
Graph 3: Basic values of mean shear bond strength of DMLS Co-Cr alloy- porcelain samples after sand blasting (Group III)



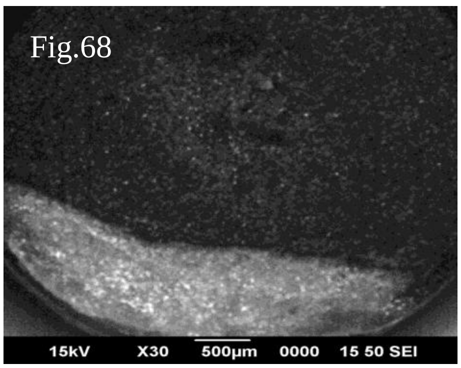
Graph 4: Basic values of shear bond strength of DMLS Co-Cr alloy-porcelain samples after laser etching (Group IV)



Graph 5: Mean shear bond strength obtained from basic values of four Groups (Group I, II, III & IV)



Qualitative analysis of Group I test samples by Scanning Electron Microscopy (SEM) under 30x and 1000x magnification and Energy Dispersive X – ray microanalysis (EDX analysis) – Fractured interface of the core surface



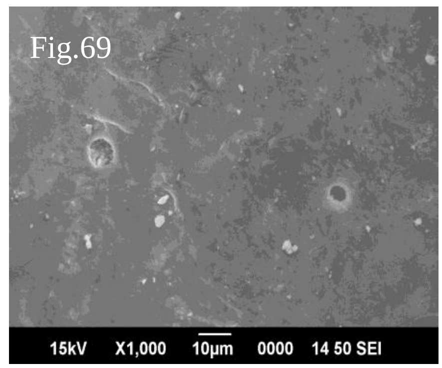
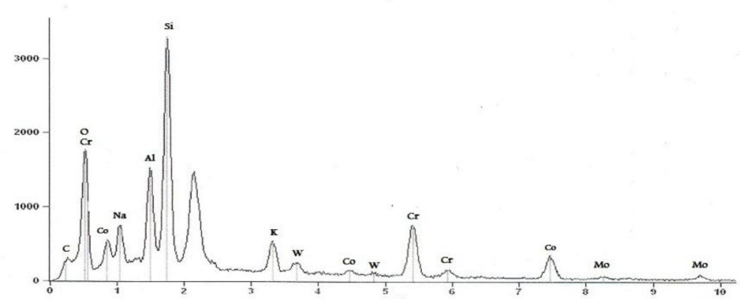


Fig.68: Debonded cast Co-Cr alloy-porcelain sample after sand balsting under 30x magnification

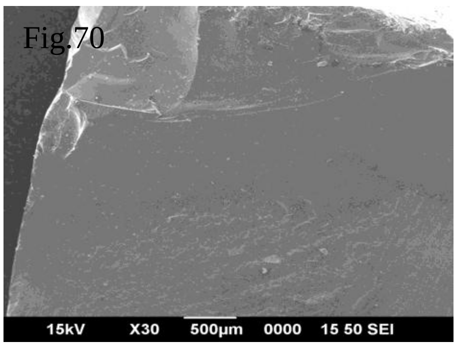
Fig.69: Debonded cast Co-Cr alloy-porcelain sample after sand blasting under 1000x magnification



Graph 6: Energy dispersive X- ray microanalysis of fractured of the core surface

(Group I)

Qualitative analysis of Group I test samples by Scanning Electron Microscopy (SEM) under 30x and 1000x magnification and Energy Dispersive X – ray micro analysis (EDX analysis) – Fractured veneer surface



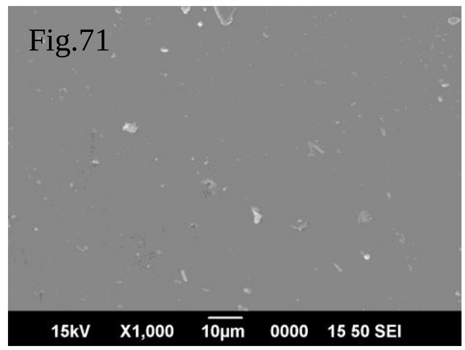
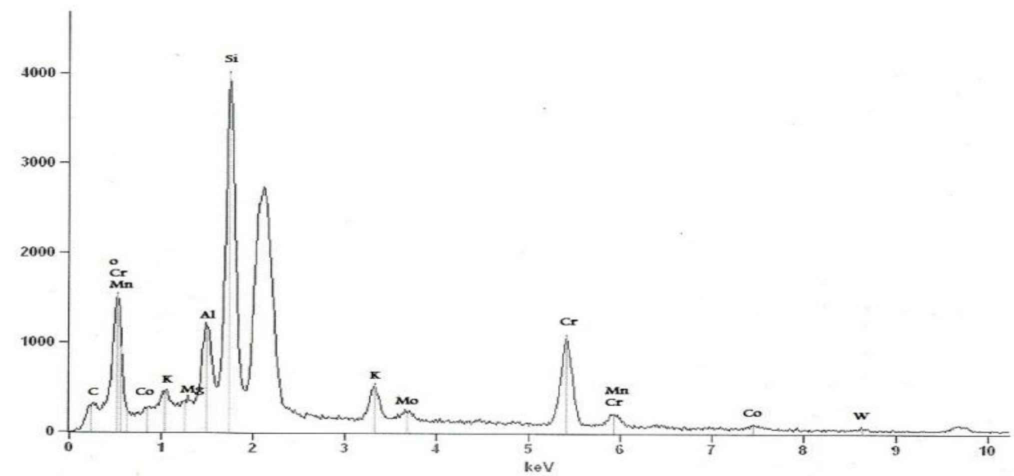


Fig.70: Fractured veneer surface Group I under 30x magnification

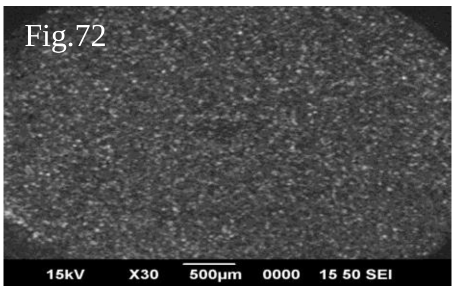
Fig.71: Fractured veneer surface Group I under 1000x magnification



Graph 7: Energy dispersive X– ray microanalysis of fractured veneer surface (Group I)

Inference (Group I): For qualitative analysis, one sample from cast Co-Cr alloy-porcelain sample after surface treatment with sand blasting (Group I) was randomly selected and examined under scanning electron microscopy (SEM) under 30x and 1000x magnifications. Under 30x and 1000x magnifications the interface of the sample revealed a predominantly cohesive failure of veneering ceramic and metal oxide. 1000x magnification showed numerous pores within the veneering ceramic and in the metal oxide interface. Chemical composition of the fractured interface was analysed using energy dispersive X-ray microanalysis (EDX analysis). Surface chemistry of the fractured interface explained the elements seen on the surface. This revealed presence of silica, alumina, chromium, cobalt, tungsten, molybdenum, sodium, potassium, magnesium, oxygen and carbon. The total count of silica was found to be higher indicating predominantly cohesive failure of veneering ceramic. Surface chemistry of fractured veneer surface revealed the presence of silica, alumina, chromium, potassium, cobalt, oxygen, tungsten magnesium and carbon. Since the percentage of silica was higher than the other elements, it indicated a predominantly cohesive failure of veneering porcelain. Graphical representation of surface chemistry was presented along with SEM images of corresponding samples.

Qualitative analysis of Group II test samples by Scanning Electron Microscopy (SEM) under 30x and 1000x magnification and Energy Dispersive X –ray microanalysis (EDX analysis) – Fractured interface of the core surface



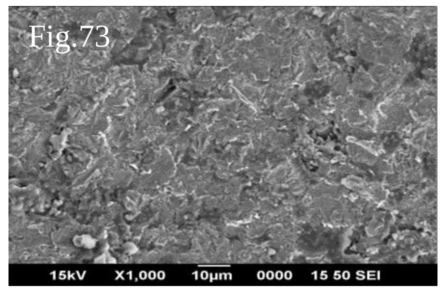
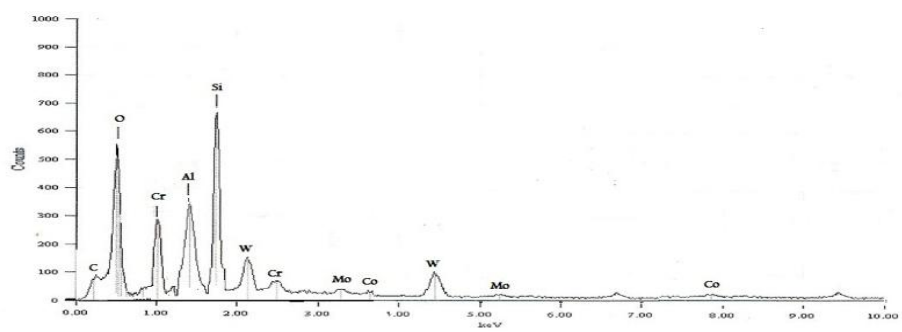


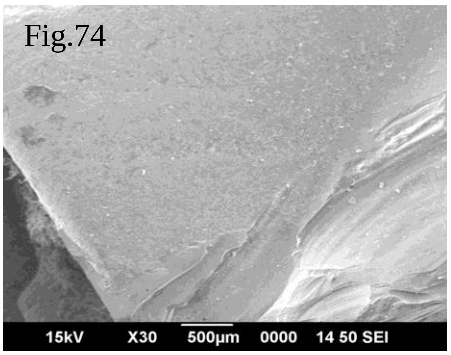
Fig 72 : Debonded cast Co-Cr alloy-porcelain sample after laser etching under 30x magnification

Fig 73 : Debonded cast Co-Cr alloy-porcelain sample after laser etching under 1000x magnification



Graph 8: Energy dispersive X-ray microanalysis of fractured interface of the core surface (Group II)

Qualitative analysis of Group II test samples by Scanning Electron Microscopy (SEM) under 30x and 1000x magnification and Energy Dispersive X – ray microanalysis (EDX analysis) – Fractured veneer surface



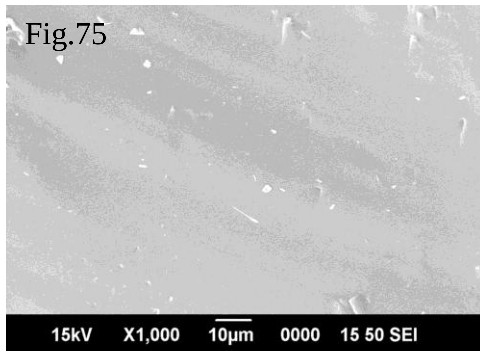
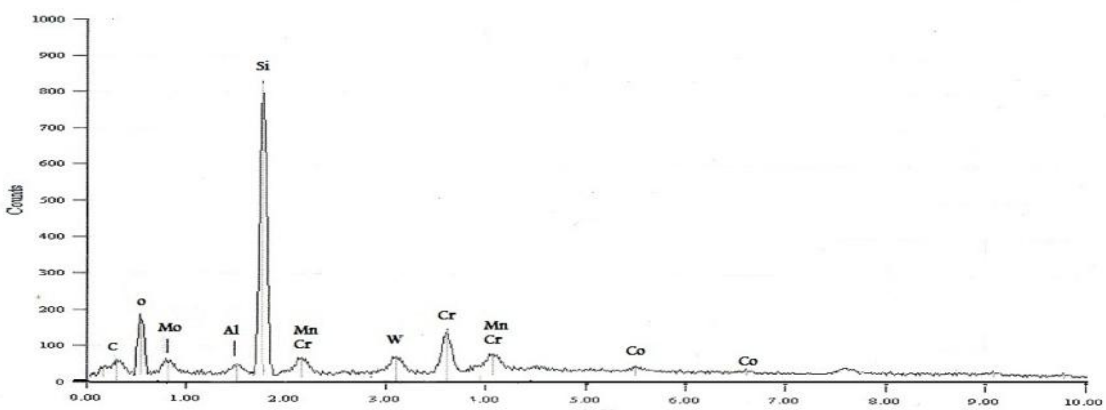


Fig.74: Fractured veneer surface (Group II) under 30x magnification

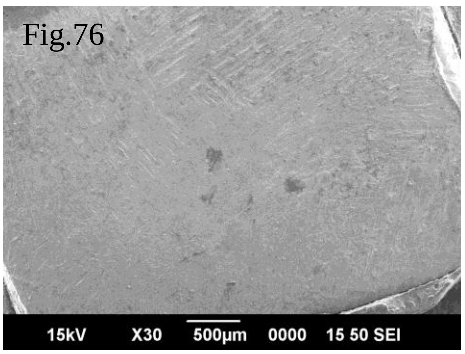
Fig.75: Fractured veneer surface (Group II) under 1000x magnification



Graph 9: Energy dispersive X-ray microanalysis of fractured veneer surface (Group II)

Inference (Group II): For qualitative analysis, one sample from the cast Co-Cr alloy-porcelain after surface treatment with laser etching (Group II), was randomly selected and examined under scanning electron microscopy under 30x and 1000x magnifications. At 30x and 1000x magnification of the interface showed predominantly cohesive failure of veneering ceramic. At 1000x, it showed small pores in the veneering ceramic layer and the alloy-porcelain interface. Chemical composition of the fractured interface was analysed using energy dispersive X-ray microanalysis (EDX analysis). Surface chemistry of the fractured interface explained the elements present in the Co-Cr alloy-ceramic and ceramic veneer. This revealed the presence of silica, alumina, chromium, cobalt, tungsten, molybdenum, oxygen and carbon. The elements seen over the fractured interface indicated cohesive failure of the veneering surface. Surface chemistry of the veneered surface revealed the presence of silica, alumina, chromium, cobalt, molybdenum, tungsten, sodium, potassium, oxygen, and carbon. Elements which were present over the fractured veneer surface also indicated cohesive failure of veneering ceramic. Graphical representation of surface chemistry was presented along with SEM images of corresponding samples.

Qualitative analysis of Group III test samples by Scanning Electron Microscopy (SEM) under 30x and 1000x magnification and Energy Dispersive X – ray microanalysis (EDX analysis) – Fractured interface of the core surface



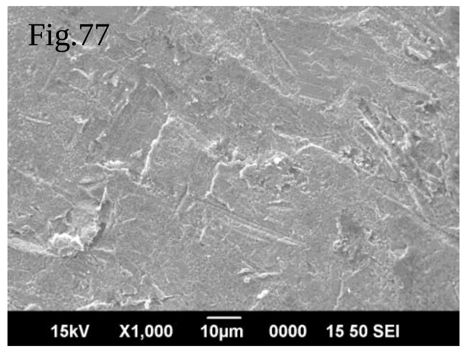
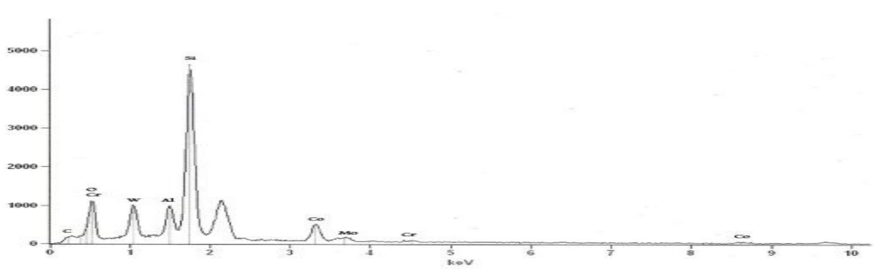


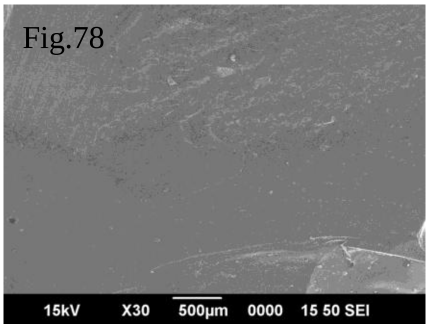
Fig.76: Debonded DMLS Co-Cr alloy-porcelain sample after laser etching under 30x magnification

Fig.77: Debonded DMLS Co-Cr alloy-porcelain sample after laser etching under 1000x magnification



Graph 10: Energy dispersive X-ray microanalysis of fracture interface of the core surface (Group III)

Qualitative analysis of Group III test samples by Scanning Electron Microscopy (SEM) under 30x and 1000x magnification and Energy Dispersive X – ray microanalysis (EDX analysis) –Fractured veneer surface



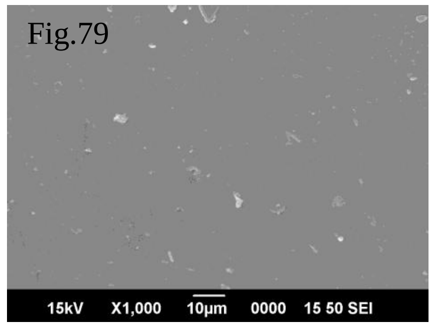
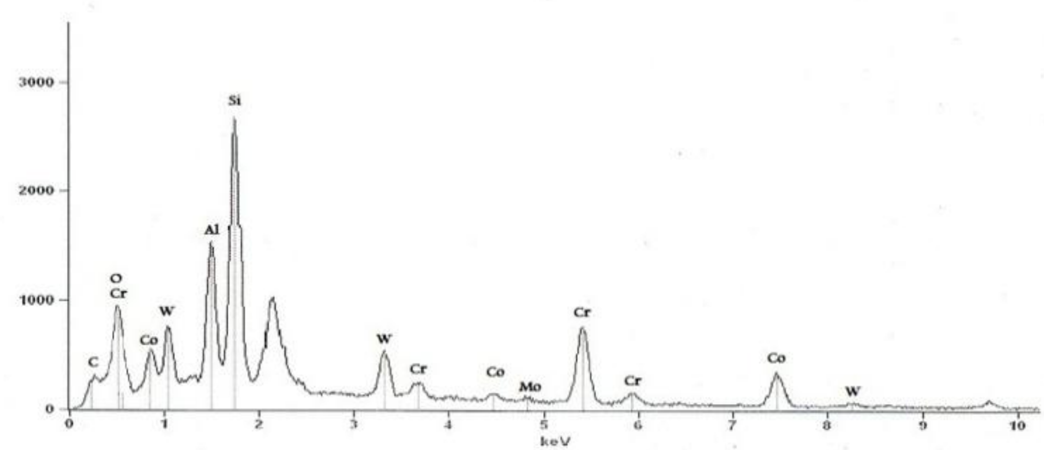


Fig.78: Fractured veneer surface (Group III) under 30x magnification.

Fig.79: Fractured veneer surface (Group III) under 1000x magnification.

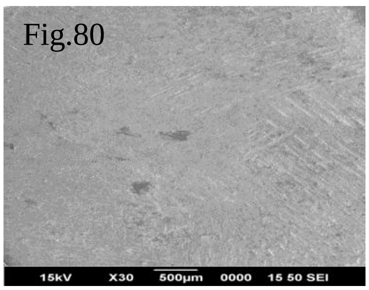


Graph 11: Energy dispersive X-ray microanalysis of fractured veneer surface

(Group III)

Inference (Group III): Qualitative analysis of DMLS Co-Cr alloy-porcelain samples after surface treatment with sandblasting was done using scanning electron microscopy. One test sample from this group was randomly selected and studied under 30x and 1000x magnifications. Under 30x magnification of tested DMLS sample after sand blasting revealed a mixed adhesive and cohesive failure of veneering ceramic. Higher magnification of 1000x shows small pores within the interface of alloy-ceramic and ceramic. Very few areas of metal were visible. Chemical composition of the fractured core surface explained the elements seen on the surface of fractured core and revealed the presence of silica, alumina, cobalt, chromium, molybdenum, tungsten, oxygen, and carbon. The elements seen on the surface of the core indicated mixed failure. Since the silica content was higher, it indicated predominantly cohesive failure of the veneering ceramic. Surface chemistry of the fractured veneer surface revealed presence of silica, alumina, chromium, molybdenum, tungsten, cobalt, oxygen carbon. Elements present over the fractured veneer indicate predominantly cohesive failure of veneering ceramic. Graphical representation of the surface chemistry was presented along with SEM images of corresponding samples.

Qualitative analysis of Group IV test samples by Scanning Electron Microscopy (SEM) under 30x and 1000x magnification and Energy Dispersive X- ray microanalysis (EDX analysis) – Fractured interface of the core surface



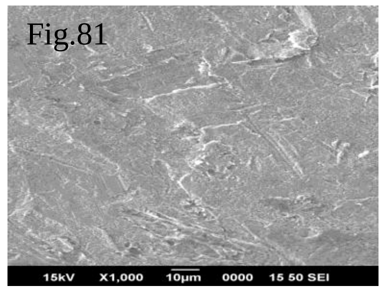
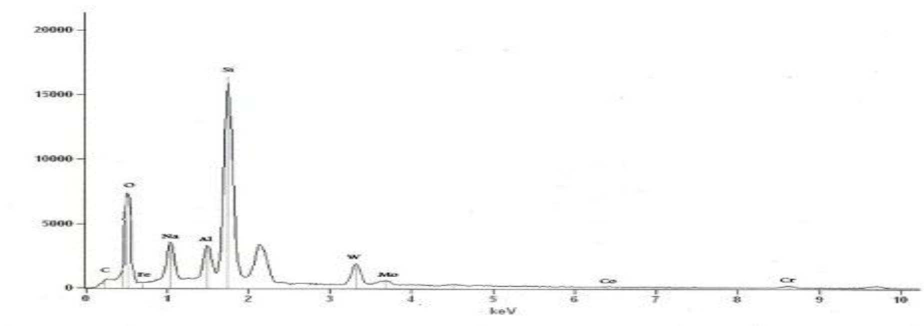


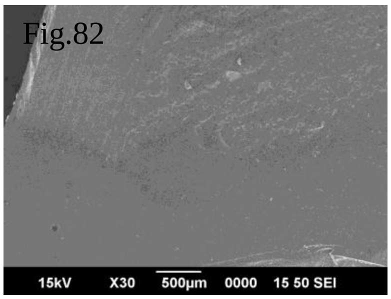
Fig.80: Debonded DMLS Co-Cr alloy-porcelain sample after laser etching under 30x magnification

Fig.81: Debonded DMLS Co-Cr alloy-porcelain sample after laser etching under 1000x magnification



Graph 12: Energy dispersive X-ray microanalysis of fractured interface of the core suface (Group IV)

Qualitative analysis of Group IV test samples by Scanning Electron Microscopy (SEM) under 30x and 1000x magnification and Energy Dispersive X – ray microanalysis (EDX analysis) – Fractured veneer surface



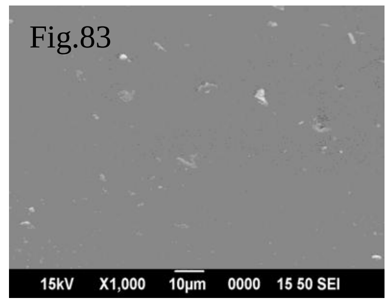
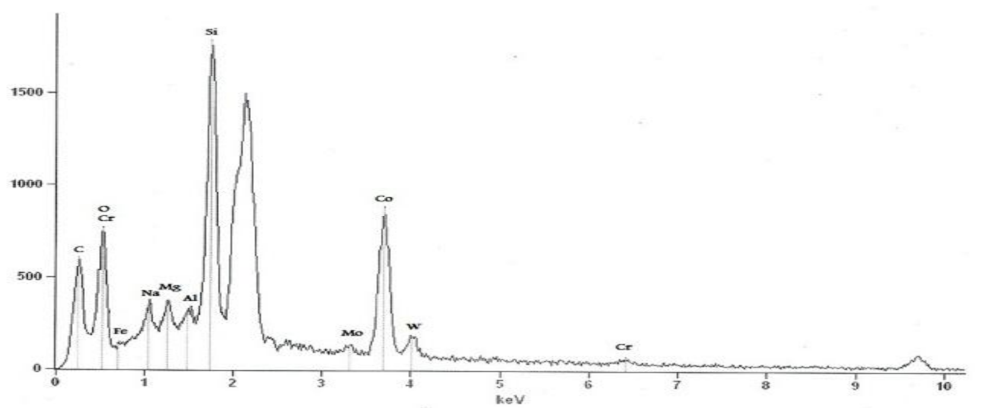


Fig.82: Fractured veneer surface (Group IV) under 30x magnification

Fig.83: Fractured veneer surface (Group IV) under 1000x magnification



Graph 13: Energy dispersive X-ray microanalysis of fractured veneer surface (Group IV)

Inference (Group IV): One DMLS Co-Cr alloy-ceramic sample after laser etching (Group IV) was randomly selected and analysed qualitatively using scanning electron microscopy under 30x and 1000x magnifications. 30 x magnifications of tested laser sintered Co-Cr samples after laser etching revealed a mixed adhesive and cohesive failure of veneering ceramic. 1000x magnification showed small pores within the veneering ceramic. Chemical composition of the fractured veneer surface was analysed using energy dispersive X-ray microanalysis (EDX analysis). Surface chemistry of the fractured interface explained the elements seen on the surface. This revealed the presence of silica, chromium, molybdenum, tungsten, cobalt, sodium, iron, carbon, and oxygen. The elements seen over the fractured interface indicated mixed failure of the veneering ceramic. Since the silica content is more, the surface chemistry indicated predominantly cohesive failure of veneering ceramic. Surface chemistry of fractured veneer surface revealed the presence of silica sodium, Chromium, magnesium, alumina, iron, cobalt, tungsten, oxygen and carbon. Elements which were present over the fractured veneer surface also indicated predominantly cohesive failure of veneering ceramic. Graphical representation of surface chemistry was presented along with SEM images of corresponding samples.

DISCUSSION

The classical method of rehabilitating partial edentulous state by means of fixed partial dental prosthesis utilizing metal-ceramic restoration is still being widely accepted.[13,16,26] The problem encountered with all-ceramic systems, commonly involves partial delamination of the veneering porcelain and sometimes fractures at the connectors.[22] Advantages of metal-ceramic restorations over all-ceramic restorations are that they require comparatively minimal tooth reduction and conventional cementation technique, where standard luting cements can be used.

The presence of metal core in the PFM restorations offers the much needed strength for its durability and thus remains standard restoration of choice in clinically demanding situations. However, the presence of metal substructure produces certain mechanical limitations, as the stress concentration at the metal-ceramic interface is found to be high and this acts as site for crack initiation and also, the mismatch of the coefficient of thermal expansion between certain alloys and the veneering porcelain makes it vulnerable to debonding at the interface.[13,18]

Alloys used in the construction of metal-ceramic restoration are noble and non-precious alloys. Non-precious alloys are commonly used in place of noble alloys, as the escalation of gold prices is a major impediment.[1,2,18]

Among the non-precious alloy, Nickel-Chromium (Ni-Cr) alloy was more often used as it possesses the desirable mechanical properties like hardness and rigidity.[13,21] The biological safety of Ni-Cr alloy was evaluated largely, as the presence of Nickel and Beryllium proved to produce allergic reactions. This has led to the use of other base metal alloys like Titanium alloys and Cobalt-Chromium (Co-Cr).[19,26] Although titanium is more biocompatible of all base metal alloys, it is highly reactive and the casting operation is technique sensitive.[11]

Co-Cr based alloys have satisfactory mechanical properties such as hardness, elasticity and tensile strength; and have shown excellent marginal integrity and an absence of adverse reactions. The conventional method of casting requires melting of the Co-Cr alloy at higher temperature and this sometimes produces thicker oxide layer, which is undesirable for porcelain bonding. Thermal contraction of the refractory mold after burnout, if not compensated adequately may lead to casting shrinkage, eventually leading to misfit of the restoration. These errors can be minimized by newer fabrication techniques like CAD-CAM milling and direct metal laser sintering (DMLS).[35]

DMLS is a newer fabrication method for the production of metal core of a fixed partial denture with Co-Cr alloy powder. DMLS is a novel, additive manufacturing process offering enhanced processing versatility, improved material properties and shortened product development cycles; it saves significant production time in the manufacture of precision made products.

The high performance, good esthetics, and high density of DMLS produced products indicate that DMLS may have a significant capacity for use in the fabrication of dental prosthesis.[51]

The longevity of metal-ceramic restorations depends on reliable bonding between metal and ceramic.[7,18] The primary determinant of the successful bond between metal and ceramic is directly related to the presence of oxide layer. However, the oxide layer should not be excessively thick as it possesses poor cohesive strength; It is a well-established fact that formation of metal oxides during oxidation is dependent on the composition of the alloy and the surface treatment rendered to the alloy.[43]

Surface treatments like sand blasting, laser etching, steam cleaning, ultrasonic cleaning, acid etching, application of bonding agent, heat treatment of the alloy, mechanical roughening with rotary instruments have been employed in order to augment the bond strength between metal and ceramic at the interface.[18] All these surface treatments were done to produce micromechanical irregularities, thereby increasing the surface area and surface energy, which is required for the successful bonding. However no standardization was found in the literature with regards to the surface treatments of metal, mainly Co-Cr, before the application of ceramic materials.[26]

In prosthodontics, sand blasting with alumina particles is extensively used for treating metallic substrates, to clean the surface of organic contaminants and to create surface irregularities that enhance mechanical bonding with veneering materials and increasing the wetting of the metallic substrate before addition of dental porcelain. It has been estimated that sand blasting increases the total surface area of a metallic substrate and also increase the metal-ceramic bond strength.[17]

The major complication of sand blasting is the retention of alumina particles on the alloy surface. The presence of such embedded fragments adversely affects the bond strength of metal-ceramic systems reducing the mechanical interlocking and also inhibiting the chemical bonding of the porcelain with the metallic oxides.[18,20]

Laser etching as a surface treatment to enhance the bond strength of Co-Cr substrate to porcelain could be an alternative to airborne particle abrasion.[20,21] Low thermal conductivity nature of Co-Cr alloys permits it to be laser treated, with production of high heat leading to rapid melting and solidification, thus producing micro irregularities on the metal surface.

In-vitro studies have been done to evaluate the metal-ceramic bond strength of Co-Cr base metal alloy subjected to conventional surface treatment like air abrasion, steam cleaning, heat treatment etc., However studies reporting on the performance of laser surface irradiation on Co-Cr alloy substructures fabricated by conventional casting and by DMLS technique are lacking. Further there is also scarcity of studies comparing the bond strength nature of metal-ceramic restorations fabricated by cast and laser sintered Co-Cr alloys.

In view of the above, the present in-vitro study was conducted for the comparative evaluation of shear bond strength of cast Co-Cr alloy and the direct metal laser sintering (DMLS) Co-Cr alloy to dental porcelain with the effect of sand blasting and laser etching surface treatments. A total of forty Co-Cr alloys specimens were fabricated by conventional casting (n=20) and by DMLS technique (n=20). The fabricated Co-Cr specimens were subjected to two different surface treatments; namely sand blasting (n=20) and laser etching (n=20). Co-Cr alloy specimens were subjected to porcelain addition in a ceramic furnace to obtain forty test samples of Co-Cr alloy fused with porcelain veneer and divided into following four groups.

Group I (n=10) cast Co-Cr alloy-porcelain test samples after surface treatment with sand blasting. Group II (n=10) cast Co-Cr alloy-porcelain test samples after surface treatment with laser etching. Group III (n=10) DMLS Co-Cr alloy-porcelain test samples with surface treatment with sand blasting. Group IV (n=10) DMLS Co-Cr alloy-porcelain test samples after surface treatment with laser etching.

Dimensions of the Co-Cr alloy–ceramic test samples employed in this present study is based on the study conducted by De Melo et al with the sample size measuring 4x4 mm cylindrical sample with a base of 5x1 mm.[7] Direct metal laser sintering (DMLS) was employed as one of the method to obtain the alloy specimens because and reasons mentioned earlier. The surface treatments followed in this study is a representative of earlier study done by Graham et al and Kim et al.[13,20] Sand blasting was chosen as it is one of the routinely used laboratory procedures for surface treatment of alloys prior to porcelain adhesion and also for reasons mentioned previously. Laser etching was chosen since sparse documentation on its effect on shear bond strength is available. The intensity of the laser used for surface etching was as per that followed in a previous study.

The test samples were mounted in universal testing machine for the evaluation of shear bond strength. The shear force at which the bond failed was recorded in Newton and the shear bond strength (MPa) was calculated by dividing the load (N) by the bonding area (mm^2). The basic values of shearbond strength obtained from the present study was tabulated and statistically analysed.

The highest shear bond strength value was obtained with DMLS Co-Cr alloy-porcelain after laser etching (Group IV 72.38 ± 0.89 MPa) followed by cast Co-Cr alloy-porcelain after laser etching (Group II 72.27 ± 0.91MPa), DMLS Co-Cr alloy-porcelain after sandblasting(Group III 71.01 ± 1.97 MPa) and the least value by cast Co-Cr alloy-porcelain after sand blasting (Group I 70.21 ± 2.69 MPa).

Group IV > Group II > Group III > Group I

The results of the present in-vitro study have shown that Co-Cr alloy test samples fabricated by DMLS technique (Gr III and Gr IV) demonstrated higher shear bond strength values compared to cast Co-Cr alloy-ceramic test samples (Gr I and Gr II) for both surface treatments, done in the study. Whereas, cast Co-Cr alloy test samples have exhibited lesser shear bond strength with both types of surface treatments. The difference in shear bond strength value between laser etched DMLS (Gr IV), sand blasted DMLS (Gr III) and cast laser etched (Gr II) test sample does not have statistical significance. However there is statistically significant difference between the shear bond strength values of laser etched DMLS (Gr IV) samples and sand blasted cast (Gr I) samples.

Further, the results of the present study have demonstrated that surface treatment with laser etching for Co-Cr alloy test samples fabricated by DMLS and casting technique have yielded higher shear bond strength compared with sand blasting. However, this increase in bond strength does not have statistical significance.

A study was conducted by Akova et al to compare shear bond strength of cast Co-Cr and laser sintered Co-Cr alloys to dental porcelain. The mean shear bond strength obtained for the cast Co-Cr alloy-ceramic was not significantly different from the DMLS Co-Cr alloy ceramic. The bond strength for cast Co-Cr alloy-ceramic was 72.29 MPa for cast Co-Cr alloys and 67.14 MPa for DMLS Co-Cr alloys. These authors in the study have concluded that DMLS Co-Cr alloy seems to be an alternative technique to conventional casting of dental alloys for porcelain fused to metal restorations.[1] The final outcome of this study is in accordance with the present study.

Xiang et al evaluated the metal ceramic bonding strength of Co-Cr alloy fabricated by selective laser melting (SLM) technique and conventional casting technique. The SLM metal ceramic system exhibit the bond strength which exceeds the required bond strength value by the ISO (25 MPa) and indicated that the alloy fabricated by SLM technique can provide an acceptable metal ceramic bond strength for clinical applications comparable to traditional casting methods. The bond strength values of Co-Cr alloy in the study were also consistent with the present study results.[51]

Air borne surface abrasion of metal surface increases the surface energy by improving the wettability of opaque porcelain and increasing the bond strength through micromechanical bonding. Aluminium oxide particles are the most common particles for this purpose. The bonding strength is dependent on the type and particle size of the air abrasion procedure. De Melo et al concluded that shear bond strength between Co-Cr alloy and porcelain ranges from 55.2 MPa to 71.7 MPa after the air abrasion surface treatment with 100 µ alumina particles.[7] Sipahi et al demonstrated the shear bond strength of Co-Cr alloy with 50µ alumina air abrasion ranges from 13. 3 to 19 MPa.[43] Kulunk et al used 50µ and 110µ alumina particles to determine the effect of alumina particle size on metal-ceramic bond strength and concluded that higher bond strength values were obtained with 110µ alumina particles.[21]

Pretti et al concluded that the shear bond strength of metal ceramic bond of Co-Cr alloy ranges from 48.3 MPa to 55.96 MPa with air abrasion surface treatment with 100µ alumina. Salazar et al evaluated the shear bond strength of Co-Cr alloy fused to ceramic after sand blasting with 100µ and reported the shear bond strength value ranges from 74.71 MPa to 76.05 MPa. Further they have stated that thermocycling did not affect the bond strength to a greater extent.[41]

Lombardo et al evaluated the influence of surface treatment with alumina air abrasion on shear bond strength between Co-Cr alloy and ceramic surface and have concluded that this type of surface treatment increases the bond strength.[26] Mehulic et al in the study demonstrated highest shear bond between Co-Cr and ceramic was obtained with 250µ alumina (66.902 MPa). This value is similar to the value obtained in the present study with 250µ alumina particle.[31]

Kim et al demonstrated that Nd:YAG laser etching with fluence of 4.9 J/cm^2 as a surface treatment to enhance the bond strength of titanium substrate to porcelain could be an alternative.[20] In this present study Nd:YAG laser with fluence of 4.9 J/cm^2 was used for laser ablation, which yielded higher bond strength values.

According to the current standards, ANSI/ADA specification No. 38(2000) and ISO Standard 9691(1999), minimum bond strengths value for metal-ceramic is 25 MPa.[5,16] According to Anusavice a minimum in vitro bond strength suggestive of an acceptable metal-ceramic bond should be 51 MPa.[1] The mean shear bond strength values found in this study for Co-Cr specimens prepared using lost wax technique and laser sintered Co-Cr specimens, surface treated with sand blasting and laser etching greatly exceeded the minimum values.

The mean shear bond strength of the Group I was (70.21 ± 2.69 MPa) which was less when compared to Group II (72.26 ±0.91 MPa). Contamination of the metal surface by alumina and excessive roughness creating stress concentrations at the metal-ceramic interface could be the reasons for this.[6] The mean shear bond strength value for Group IV (72.37 ± 0.89 MPa) was higher than other groups and statistically significant than Group I, this could be due to the fact that the laser etched surface is less contaminated prior to ceramic addition and also the composition of Co-Cr alloy used for DMLS has lower molybdenum content compared to that of Co-Cr alloy used for conventional casting. Presumably, laser sintering alloy is facilitated by the absence of such refractory metals which have higher melting range than cobalt and chromium. Further research would be of great use in these areas.

Results of shear bond strength of this present study (70.21- 72.37 MPa) from all 40 specimens were higher than the acceptable range and in consensus with those of Akova, Joias, Mehulic and de Melo.

Qualitative analysis of mode of failure of samples were analysed by scanning electron microscope under 30x and 1000x magnifications. The analysis was done for both the fractured interface and the fractured veneering porcelain for all test groups. Interface and veneering porcelain surface chemistries were evaluated using energy dispersive X–ray microanalysis. These were done to correlate the failure mode of test samples and corroborate them with the surface chemistry analysis.

For qualitative analysis, one sample from cast Co-Cr alloy samples after surface treatment with sand blasting (Group I) was examined under scanning electron microscopy (SEM) under 30x and 1000x. Under both 30x and 1000x magnifications a predominantly cohesive failure both at the interface and veneering porcelain was observed. Chemical composition of the fractured interface was analysed using energy dispersive X-ray microanalysis (EDX analysis). This revealed presence of silica, alumina, chromium, cobalt, sodium, potassium, magnesium, oxygen and carbon in both fractured surfaces. The higher percentage of silica indicated a predominantly cohesive failure of veneering ceramic and corroborated with the SEM findings.

For qualitative analyses of the conventional cast Co-Cr alloy after surface treatment with laser etching (Group II), one sample was randomly selected and studied under scanning electron microscopy under 30x and 1000x. Under both 30x and 1000x magnifications a predominantly cohesive failure both at the interface and veneering porcelain was observed. Higher magnification at 1000x showed small pores in the veneering ceramic layer and the alloy surface. Chemical composition of the fractured interface was analysed using energy dispersive X-ray microanalysis (EDX analysis) revealed the presence of silica, alumina, chromium, cobalt, sodium, potassium, oxygen and carbon on both the fractured surfaces. The elements seen over the fractured interface indicated cohesive failure of the veneering surface, thus corroborating with the SEM findings.

Qualitative analyses of the DMLS Co-Cr alloy samples surface treated with sandblasting was done using scanning electron microscopy. One test sample from this group was randomly selected and studied under 30x and 1000x magnification. Under 30x and 1000x magnifications the sample revealed a mixed adhesive and a predominantly cohesive failure of veneering ceramic. Chemical composition of the fractured core surface explained the elements seen on the surface of fractured core and revealed the presence of silica, alumina, sodium, potassium, oxygen, and carbon on both the fractured surfaces. The elements seen on the surface of the core indicated mixed failure. Since the silica content was higher, it indicates predominantly cohesive failure of the veneering ceramic. This matched with the SEM observations.

One DMLS Co-Cr alloy sample after surface treatment with laser etching (Group IV) was randomly selected and analysed qualitatively using scanning electron microscopy under 30x and 1000x. These magnifications of tested laser sintered Co-Cr samples after laser etching revealed a mixed adhesive and cohesive failure of veneering ceramic. Chemical composition of the fractured interface as well as the veneer surface was analysed using energy dispersive X-ray microanalysis (EDX analysis). This revealed the presence of silica, sodium potassium, carbon, and oxygen on both the fractured surfaces. The elements seen over the fractured interface indicated mixed failure of the veneering ceramic and were in correlation with the SEM observations.

Kulunk et al[21] studied the fractured interfaces of Ni-Cr and Co-Cr alloy specimens subjected to air abrasion using SEM. Their results revealed a predominantly adhesive mode of failure. This is in contrast to the predominantly cohesive failure observed in the present study. This can be attributed to the smaller grit sizes of 50 µm and 110 µm of alumina employed in their study. The grit size of 250 µm employed in the present study may account for improved bonding resulting in cohesive failure at the interface. This is suggestive of a stronger oxide layer than the veneering ceramic.

These findings are also in accordance with those observed by Graham et al.[13] Their SEM observations revealed a predominantly cohesive failure within the porcelain indicating that the metal-oxide interface was stronger than the porcelain. They attributed this to the presence of porosities due to entrapped air within the porcelain and also due to contamination of porcelain. The presence of visible pores as observed under higher magnification in the present study is also suggestive of the same.

Within the limitations of the present study, on overall comparison, specimens obtained by DMLS technique exhibited higher shear bond strength values as compared to those obtained by conventional casting procedures. Among the two surface treatments tested, laser etching resulted in higher shear bond strength values for both methods of fabrication.

The predominantly cohesive and mixed modes of failure indicate good bond strength between the Co-Cr alloy substrates and porcelain, among all groups tested. The qualitative assessment of the present study is in correlation with the quantitative results obtained.

The present study had some limitations. The design of the specimens did not replicate the clinical situations and also a static test was performed without thermocycling procedures as in actual oral environment, where there would be repeated changes of temperatures and pH. Hence, specimens replicating clinical situations and tested under dynamic load conditions after thermocycling procedure should be included in the subsequent studies. As for as the laser surface treatment, only one energy level of laser fluence (4.9 J/cm^2) was employed and Co-Cr was the only alloy tested.

As the veneering ceramic material is weak compared to the high strength core material, the veneering ceramic is prone to fail at low loads. Thus all tested samples fractured predominantly as cohesive failure. This type of failure mode indicated a sufficient interfacial bond between the core and veneer material. The cohesive failure of veneering ceramic strongly suggests high residual stresses within the veneer layer. This may be related to the varying thermal diffusivity of core and veneer material. The mismatch in coefficient of thermal expansion may lead to different stress states in the two systems. The effect of coefficient of thermal expansion and the highly deleterious impact on core and veneer ceramics caused by residual stresses has been frequently discussed in the dental literature.

Since the bond strength of the interface was higher than the cohesive strength of the veneering ceramic, it was concluded that the veneering ceramic was the weakest link. Improving the strength of the veneering ceramic and curbing porcelain contamination may reduce the failure and is important to the longevity of the restoration.

Future studies focusing on the effect of varying the laser fluence on the shear bond strength along with other surface treatment tested simultaneously on the base metal alloys are recommended to add merit to the conclusions obtained with the present study.

CONCLUSION

The present in vitro study was conducted for the comparative evaluation of shear bond strength of cast Co-Cr alloy and direct metal laser sintering (DMLS) Co-Cr alloy to dental porcelain with the effect of sand blasting and laser etching surface treatments.

1. The mean shear bond strength obtained with the cast Co-Cr alloy-porcelain test samples after surface treatment with sand blasting (Group I) was found to be 70.21 ± 2.69 MPa.
2. The mean shear bond strength obtained with the cast Co-Cr alloy-porcelain test samples after surface treatment with laser etching (Group II) was found to be 72.26 ± 0.91 MPa
3. The mean shear bond strength obtained with DMLS Co-Cr alloy-porcelain test samples after surface treatment with sand blasting (Group III) was found to be 71.00 ± 1.97 MPa.
4. The mean shear bond strength obtained with DMLS Co-Cr alloy-porcelain test samples after surface treatment with laser etching (Group IV) was found to be 72.37 ± 0.89 MPa.
5. On comparison the mean shear bond strength obtained with cast Co-Cr alloy-porcelain test samples after surface treatment with sand blasting (Group I) and laser etching (Group II), were found to be 70.21 ± 2.69 MPa

and 72.26 ± 0.91 MPa respectively. The mean shear bond strength value was found to be higher with Group II (laser etched group). The increase in shear bond strength value does not show statistical significance.

6. On comparison, the mean shear bond strength obtained with cast Co-Cr alloy- porcelain (Group I) and DMLS Co-Cr alloy porcelain (Group III) test samples after surface treatment with sand blasting were found to be 70.21 ± 2.69 MPa and 71.00 ± 0.91 MPa respectively. The mean shear bond strength value was found to be higher with DMLS samples. The increase in shear bond strength does not show statistical significance.

7. On comparison between the mean shear bond strength obtained from cast Co-Cr alloy-porcelain test samples after alloy surface treatment with sand blasting (Group I- 70.21 ± 2.69 MPa) and DMLS Co-Cr alloy-porcelain after alloy surface treatment with laser etching (Group IV- 72.37 ± 0.91 MPa), the mean shear bond strength value was found to be higher in DMLS samples. The increase in shear bond strength value shows statistical significance.

8. On comparison between the mean shear bond strength obtained with cast Co-Cr alloy-porcelain samples after surface treatment with laser etching (Group II - 72.26 ± 0.91 MPa) and DMLS Co-Cr alloy-porcelain samples after surface treatment with sand blasting (Group III- 71.00 ± 1.97 MPa),

the mean shear bond strength value was found to be decreasing in sand blasted group (Group III). The decrease in shear bond strength was statistically not significant.

9. On comparison, the mean shear bond strength obtained with cast Co-Cr alloy-porcelain (Group II) and DMLS Co-Cr alloy-porcelain (Group IV) test samples after the alloy surface treatment with laser etching were found to be 72.26 ± 0.91 MPa and 72.37 MPa respectively. The mean shear bond strength value was found to be higher with the laser etched group (Group IV). The increase in shear bond value does not show statistical significance.
10. On comparison between the mean shear bond strength obtained with DMLS Co-Cr alloy-porcelain test samples after the surface treatment with sand blasting (Group III –71.00 ± 1.97 MPa) and after laser etching (Group IV –72.37 ± 0.89 MPa), the bond strength value was found to be higher with laser etching and the difference was found to be statistically insignificant.
11. On overall comparison, the highest shear bond strength value was obtained with DMLS Co-Cr alloys-porcelain test samples after laser etching (Group IV –72.38 ± 0.89 MPa), followed by cast Co-Cr alloy-porcelain test samples after laser etching (Group II –72.27 ± 0.91 MPa), DMLS Co-Cr alloy-porcelain test samples after sand blasting (Group III –

71.01 ± 1.97 MPa) and the least by cast Co-Cr alloy-porcelain after sand blasting (Group I –70.21 ± 2.69 MPa).

Group IV > Group II > Group III > Group I

Statistical analysis by one way Anova showed statistically significant difference among the four groups tested. (P-Value = 0.027). As the one-way Anova analysis showed significant results, post-hoc Tukey HSD analysis was done for multiple comparisons within the groups. This analysis showed no statistically significant difference within the groups studied except within group I and IV which showed statistical significance.

12. SEM and EDX analysis of one test sample from each test group revealed the following:

Group I – SEM analysis under 30x and 1000x magnifications revealed predominantly cohesive failure within the veneering porcelain. EDX analysis exhibited higher content of silica on the fractured core surface and also on the fractured veneer surface indicative of predominantly cohesive failure of the veneering porcelain.

Group II- SEM analysis under 30x and 1000x magnifications revealed predominantly cohesive failure of veneering porcelain. EDX analysis demonstrated higher content of silica on fractured core surface and fractured veneer surface indicated cohesive failure of veneering porcelain.

Group III- SEM analysis under 30x and 1000x magnifications revealed a mixed cohesive and adhesive failure of veneering porcelain, with predominantly cohesive failure of veneering ceramic. EDX analysis showed high content of silica on fractured veneer surface indicative of predominantly cohesive failure of veneering porcelain.

Group IV- SEM analysis under 30x and 1000x magnifications revealed a mixed cohesive and adhesive failure of veneering porcelain, with predominantly cohesive failure of veneering porcelain. EDX analysis exhibited higher content of silica on fractured core surface and fractured veneer surface indicating predominantly mixed failure of veneering porcelain.

The predominantly cohesive and mixed modes of failure indicates good bond strength between the Co-Cr alloy substrates and porcelain, among all groups tested. This qualitative assessment of the present study is in correlation with the quantitative results obtained.

SUMMARY

The present in vitro study was conducted for the comparative evaluation of shear bond strength of cast Co-Cr alloy and the direct metal laser sintering (DMLS) Co-Cr alloy to dental porcelain with the effect of sand blasting and laser etching surface treatments.

A total of forty (n=40) Co-Cr alloy specimens were fabricated by conventional casting and DMLS techniques. The alloy surfaces were treated with sand blasting and laser etching, and porcelain was fused to the treated surface. The test samples of Co-Cr alloy-porcelain were grouped as Group I, II, III and IV of ten (n=10) in each group based on the technique of alloy fabrication and method of surface treatments. All samples were tested for shear bond strength in Universal testing machine. The shear bond strength was calculated, tabulated and statistically analysed. Tested samples were qualitatively analysed with scanning electron microscope (SEM) and energy dispersive spectrometer (EDS).

The results in the present in vitro study revealed that the highest shear bond strength was obtained with DMLS Co-Cr alloy-porcelain after laser etching (Group IV 72.37 ± 0.89 MPa) followed by cast Co-Cr alloy- porcelain after laser etching (Group II 72.26 ± 0.91 MPa), DMLS Co-Cr alloy-porcelain after sand blasting (Group III 71.00 ± 1.97 MPa) and the least by cast Co-Cr alloy-porcelain after sand blasting (Group I 70.21 ± 2.69 MPa).

Group IV > Group II > Group III > Group I.

The results of the present in-vitro study have shown that a Co-Cr alloy test samples fabricated by DMLS technique (Gr III and Gr IV) demonstrated higher shear bond strength values compared to cast Co-Cr alloy-porcelain test samples (Gr I and Gr II) for both surface treatments, done in the study. The difference in shear bond strength value between laser etched DMLS (Gr IV), sand blasted DMLS (Gr III) and cast laser etched (Gr II) test sample does not have statistical significance. However there is statistical significance found between laser etched DMLS (Gr IV) samples and sand blasted cast (Gr I) samples.

Further, the results of the present study have demonstrated that surface treatment with laser etching for Co-Cr alloy test samples fabricated by DMLS and casting technique have yielded higher shear bond strength compared with sand blasting. The increase in bond strength does not have statistical significance.

It was evidenced that laser etching had an influence on the shear bond strength of cast Co-Cr alloy-porcelain and as well as DMLS Co-Cr alloy-porcelain samples. Laser etching improved the shear bond strength of cast and DMLS Co-Cr alloy-porcelain and the maximum shear bond strength was obtained with the DMLS Co-Cr alloy-porcelain test samples. The improvement (increase) in shear bond strength with laser etched surfaces does not show statistical significant difference compared to sand blasting with DMLS groups but statistical significance exists with the cast group.

Upon SEM analysis, Group I samples revealed cohesive failure of alloy-porcelain bonding, predominantly failure within the veneering porcelain. Group II samples revealed cohesive failure of veneering porcelain. Group III samples revealed mixed cohesive and adhesive failure of veneering porcelain, predominantly cohesive failure of veneering porcelain. Group IV samples revealed mixed cohesive and adhesive failure of veneering porcelain, predominantly cohesive failure of veneering porcelain. The EDX analysis obtained for each group was also in correlation with SEM observations.

The predominantly cohesive and mixed modes of failure indicate good bond strength between the Co-Cr alloy substrates and porcelain, among all groups tested. The qualitative assessment of the present study is in correlation with the quantitative results obtained.

This present study shows that laser sintering the Co-Cr alloy powder to form the substructure of alloy- porcelain restoration after the surface treatment of laser etching have exhibited the maximum shear bond strength that exceeds the requirement of ISO 9691:1999. This indicates that the alloy fabricated by DMLS can provide acceptable alloy-porcelain bond strength for clinical applications comparable to traditional cast methods. Thus the new direct metal laser sintering (DMLS) technique for Co-Cr alloy appears promising for dental applications but additional studies on the properties of DMLS alloy and fit of castings prepared by this new technique are needed before its acceptance into dental practice.

BIBLIOGRAPHY

1. **Akova Tolga, Ucar Yurdanur, Tukay Alper, Balkaya Mehmet Cudi, Brantley A William**. Comparison of the bond strength of laser – sintered and cast base metal dental alloys to porcelain. Dental Materials 2008; 24:1400-1404.
2. **Aladag Akin, Comlekoglu M. Erhan, Dundar Mine, Gungor M. Ali, Artunc Celal.** Effects of soldering and laser welding on bond strength of ceramic to metal**.** J Prosthet Dent 2010;105:28-34.
3. **Anusavice K. J., Dehoff P. H., and Fairhurst C. W.** Comparative evaluation of ceramic-metal bond tests using finite element stress analysis. J Dent Res 1980;59:608-613.
4. **Anusavice K. J., Ringle Robert D., and Fairhurst Carl W.** Adherence controlling elements in ceramic-metal systems. II. Nonprecious Alloys.J Dent Res 1977;56(9):1053-1061.
5. **Bondioli R. Ilda, Bottino Marco Antonio.** Evaluation of shear bond strength at the interface of two porcelain and pure titanium injected into the casting mould at three different temperatures. J Prosthet Dent 2004;91:541-7.
6. **Carpenter Michael A., and Goodkind Richard J.** Effect of varying surface texture on bond strength of one semiprecious and one nonprecious ceramo-alloy. J Prosthet Dent 1979; 42: 86-95.

7. **De Melo Renata Marques, Travassos Alessandro Caldas, and Neisser Maximiliano Piero.** Shear bond strengths of a ceramic system to alternative metal alloys. J Prosthet Dent 2005;93:64-9.

8. **De Vasconcellos Luis Gustavo Oliveira, Buso Leonardo, Lombardo Geraldo H. L., Souza Rodrigo O. A., Junior Lafayette Nogueira, Bottino Marco Antonio, and Ozcan Mutlu.** Opaque Layer Firing Temperature and Aging Effect on the Flexural Strength of Ceramic Fused to Cobalt-Chromium Alloy. Journal of Prosthodontics 2010;19:471–477.

9. **De Vasconcellos Luis Gustavo Oliveira, Lucas H. Silva, Luana Marotta Reis de Vasconcellos, Ivan Balducci, Fernando E. Takahashi, & Marco Antonio Bottino**. Effect of Airborne-Particle Abrasion and Mechanico-Thermal Cycling on the Flexural Strength of Glass Ceramic Fused to Gold or Cobalt–Chromium Alloy. Journal of Prosthodontics 2011;20:553–560.

10. **Fischer J.** Ceramic bonding to a dental gold – titanium alloy. Biomaterials 2002;23:1303-311.

11. **Galo Rodrigo, Frizzas Deborah Ganga, Rodrigues Renata Cristina Silvira, Rebeiro Ricardo Faria, mattos Maria Da Gloria Chiarello De**. Shear bond strength of dental ceramics to cast commercially pure titanium. Braz. J.Oral science 2010;9(3).

12. **Gilbert L. Jeremy, Covey A. David, Lautenschlager P. Eugene.** Bond characteristics of Porcelain fused to milled titanium. Dent Mater; 1994;10:134-140.

13. **Graham Julia D, Antbony fobnson, David C. Wildgoose, Mobammed Y. Sbareef, Giuseppe Cannavina.** The Effect of Surface Treatments on the Bond Strength of a Nonprecious Alloy-Ceramic Interface. Int Prosthodont 1999;12:330-334.

14. **Graiff Lorenzo, Caterina Piovan, Paolo Vigolo, & Pier Nicola Mason.** Shear Bond Strength between Feldspathic CAD/CAM Ceramic and Human Dentine for Two Adhesive Cements. Journal of Prosthodontics 2008;17:294–299.

15. **Haag Per & Nilner Krister.** Bonding between titanium and dental porcelain: A systematic review. Acta Odontologica Scandinavica 2010;68:154–164.

16. **Haselton R. Debra, Diaz-Arnold M. Ana, and Dunne T. James, Jr.** Shear bond strengths of 2 intraoral porcelain repair systems to porcelain or metal substrates. J Prosthet Dent 2001;86:526-31.

17. **Hofstede M.Theresa., Ercoli Carlo, Graser N. Gerald, Ross H., Moss E. Mark, and Zero T. Domenick.** Influence of metal surface finishing on porcelain porosity and beam failure loads at the metal-ceramic interface. J Prosthet Dent 2000;84:309-17.

18. **Hussaini Ibrahim Al, and Al Wazzan A. Khalid**. Effect of surface treatment on bond strength of low-fusing porcelain to commercially pure titanium. J Prosthet Dent 2005;94:350-6.

19. **Joias Renato Morales, Tango Rubens Nisie, Araujo Jose Eduardo Junho de, Araujo Maria Amelia Junho de, Saavedra Guilherme de Siqueira Ferreira Anzaloni, Arruda Paes-JuniorTarcisio Jose de, and Kimpara Estevao Tomomitsu.** Shear bond strength of a ceramic to Co-Cr alloys. J Prosthet Dent 2008;99:54-59.

20. **Kim Jin-Tae, and ChoSung-Am**. The effects of laser etching on shear bond strength at the titanium ceramic interface. J Prosthet Dent 2009;1:101-106.

21. **Kulunk Tolga, Murat Kurt, Cagrı Ural, Safak Kulunk, Seniha Baba.** Effect of different air-abrasion particles on metal-ceramic bond strength. Journal of Dental Sciences 2011;6:140-146.

22. **Larsson C, Holm L.** Fracture strength of four–unit Y-TZP FPD cores designed with varying connector diameter- An vitro study. Journal of Oral Rehab 2007;34:702-709.

23. **Lenz Jurgen, Kessel Siegfried**. Thermal stresses in metal–ceramic specimens for the ISO crack initiation test (three-point flexure bond test) Dent Mater 1998;14:277–280.

24. **Lim Hyun-Pil, Kim Ji-Hye, Lee Kwang-Min, Park Sang-Won.** Fracture load of titanium crowns coated with gold or titanium nitride

and bonded to low fusing porcelain. J Prosthet Dent 2011;105:164-170.

25. **Liu Jie, Atsuta Mitsura and Watanabe Ikaya.** Bond strength of Porcelain to degassed cast titanium. Int Chin J Dent 2002;2:67-74.

26. **Lombardo Geraldo H. L, Renato S. Nishioka, Rodrigo O. A. Souza, Silvia M. A. Michida, Alberto N. Kojima, Alfredo M. M. Mesquita, & Leonardo Buso.** Influence of Surface Treatment on the Shear Bond Strength of Ceramics Fused to Cobalt–Chromium. Journal of Prosthodontics 2010;19:103–111.

27. **Lubovich P.Ronald, Goodkind J. Richard.** Bond strength studies of precious, semi- precious and non precious ceramic- matal alloys with two porcelains. Prosthet Dent 1977;37:288- 299.

28. **Madani S. Azam, Rokni Shahin Rezaii, Mohammadi Abolghasem, & Bahrami Mehran**. The Effect of Recasting on Bond Strength between Porcelain and Base-Metal Alloys. Journal of Prosthodontics 2011;20:190–194.

29. **Madhav VNV, Padmanabhan TV, Subramanian R.** Evaluation of flexural bond strength of porcelain to used nickel- chromium alloy in various percentages. Indian journal of dental research 2012;23:1.

30. **Malhotra L. Manohar L., and Maickel B.Lawrence, J. Aderer,** Shear bond strength in porcelain-metal restorations. The journal of prosthodontics 1980;44(4):397-400.

31. **Mehulić Ketij, Martina Lauš-Šošić, Zdravko Schauperl, Denis Vojvodić, Sanja Štefančić.** Influence of cast surface finishing process on metal-ceramic bond strength. Medicinski glasnik 2009;6:2.

32. **Murray K. Andrea, Attrillb C.David, Dickinsona R. Mark.** The effects of XeCl laser etching of Ni–Cr alloy on bond strengths to composite resin: a comparison with sandblasting procedures. Dental Materials 2005;21:538–544.

33. **Neto Alfredo Julio Fernandos, Panzeri Heitor, Neves Flavio Domingues, Prado Ricardo Alves do, Mendonca Gustavo.** Bond Strength of Three Dental Porcelains to Ni-Cr and Co-Cr-Ti Alloys. Braz Dent J 2006;17:24-28.

34. **Oh.W, Gotzen N and Anusavice K.J**, Influence of connector design on fracture probability of ceramic Fixed-Partial Dentures. J Dent Res 2002;81:623-627.

35. **Ortorpa Anders, David Jönssonb, Alaa Mouhsenb, Per Vult von Steyernb.** The fit of cobalt–chromium three-unit fixed dental prostheses fabricated with four different techniques: A comparative in vitro study. Dental materials 2011;27:356–363.

36. **Oyafuso Denise Kanashiro, Ozcan Mutlu, Bottino Marco Antonio, Itinoche Marcos Koiti.** Influence of thermal and mechanical cycling on the flexural strength of ceramics with titanium or gold alloy frameworks. Dental materials 2008;24:351-356.

37. **Ozcan. M**. Evaluation of alternative intra-oral repait techniques for fractured ceramic-fused-to-metal restorations. Journal of Oral Rehab 2003;30:194-203.

38. **Padrós L. Jose, Padrós Eduardo, Keogh P. Thomas, and Monterrubio Margarita.** New method for the in vitro evaluation of dental alloy bonding systems. J Prosthet Dent 2000;84:217-21.

39. **Pecora Nikole, Yaman Peter, Dennison Joseph, and Herrero Alberto.** Comparison of shear bond strength relative to two testing devices. J Prosthet Dent 2002;88:511-5.

40. **Roberts W. Howard, Berzins W. David, Keith Moore, & Charlton G David.** Metal-Ceramic Alloys in Dentistry: A Review. Journal of Prosthodontics 2009;18:188–194.

41. **Salazar M. Susana, Pereira MB.Sarina, CcahuanaV Z. Vanessa, Passos P. Sheila, Vanderlei D. Aleska, Pavanelli A Carlos, Battino A Marco.** Shear bond strength between metal alloy and a ceramic system, submitted to different thermocycling immersion times. Acta Odontol, Latinoam 2007;20:97-102.

42. **Silver Milton, George Klein, and Michael C. Howard.** An evaluation and comparison of porcelains fused to cast metals. J Prosthet Dent 1960;10:1055-1064.

43. **SIPAHI Cumhur and Mutlu ÖZCAN.** Interfacial shear bond strength between different base metal alloys and five low fusing

feldspathic ceramic systems. Dental Materials Journal 2012;31(3):333–337.

44. **Tara Milia Abou, Stephanie Eschbach, Frank bohlsen, Matthias Kern.** Clinical Outcome of Metal- Ceramic Crowns Fabricated with Laser-Sintering Technology. Int J prosthodont 2011;24:46-48.

45. **Stephane Viennot, Francis Dalard, Guillaume Malquarti, and Brigitte Grosgogeat.** Combination fixed and removable prostheses using a CoCr alloy: A clinical report. J Prosthet Dent 2006;96:100-3.

46. **Wataha John C.** Alloys for prosthodontic restorations. J Prosthet Dent 2002;87:351-63.

47. **Wataha John C.** Biocompatibility of dental casting alloys: A review J Prosthet Dent 2000;83:223-34.

48. **White Shane N., Ly Ho, Angelo A. Caputo and Edward Goo.** Strength of porcelain fused to titanium beams. J Prosthet Dent 1996;75:640-8.

49. **Wight Thomas A., John C. Bauman, and George B., Pelleu.** An evaluation of four variables affecting the bond strength of porcelain to nonprecious alloy. J Prosthet Dent 1977:37(5)570-77.

50. **Wood Marjorie C. Geoffrey A. Thompson, John R. Agar.** A comparison of debonding strengths of four metal ceramic systems with and without opaque porcelain. J Prosthet Dent 2007;97:141-9.

51. **Xiang Nan, Xian-Zhen Xin, Jie Chen, Bin Wei.** Metal–ceramic bond strength of Co–Cr alloy fabricated by selective laser melting. Journal of dentistry 40(2012)453–457.