

## EFFECT OF SURFACE TREATMENT ON RESIN BONDING TO 3D PRINTED CO-CR DENTAL ALLOY

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### ABSTRACT

**Objectives:** The bond strength of resin cements to 3D printed Cobalt-Chromium alloys has not been thoroughly studied.

The study compared three different surface treatment methods on the shear bonding of adhesive resin cement to laser sintered Co-Cr alloy. The surface treatment methods were blasting with 30 $\mu$ m alumina chemically modified with silica (Cojet sand) for group A, fine 50 $\mu$ m and 110 $\mu$ m aluminum oxide blasting for groups B and C respectively.

**Materials and Methods:** Thirty disk-shaped samples of 8mm diameter and 3mm thickness were manufactured of 3D printed (laser sintered) Co-Cr alloy, then were wet ground with 200-1000-grit silicon carbide abrasive then polished. Disks were divided to three groups according to the selected surface treatment method. Self adhesive resin cement disks of 5mm diameter were bonded to the alloy samples with the aid of a Teflon mold following manufacturer's instructions. Bonded samples were thermocycled (2000 cycles between 5° and 55°C, 30 seconds dwell time) to simulate fluctuation of temperature within the oral cavity. Then, shear bond test was performed and mode of failure was inspected.

**Results:** debonding numericals were analyzed using one-way ANOVA followed by Tukey's post hoc test. The significance level was set at  $p < 0.05$  within all tests. Shear bond values were greater when sandblasting with aluminum oxide was used (12.35 $\pm$ 1.53 and 11.85 $\pm$ 1.41) MPa, compared with silica blasting (6.84 $\pm$ 1.14) MPa. A combined failure mode (adhesive-cohesive) was encountered at the resin cement –alloy interface.

**KEYWORDS:** 3D printed, Resin Bonding, Surface Treatment

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## INTRODUCTION

In the past few decades, digitalized technologies have been employed extensively in all aspects of dentistry. The employment of CAD/CAM systems has long been directly associated with the milling of pre-manufactured materials. However, now days, some CAD/CAM systems employ Laser sintering either, direct laser melting (DMLS) or selective laser sintering (SLS) for the production of polymeric, ceramic as well as metallic restorations, aiming to avoid the distortions inherent to casting procedures.<sup>(1)</sup>

Over the years cobalt-chromium alloy have been extensively used in fabricating multi-unit fixed partial denture frameworks or superstructures for dental implants. Their excellent corrosion resistance, biocompatibility and strength have demonstrated a remarkable level of versatility and durability. However, they are more difficult to be manufactured via lost wax technique, as casting inaccuracy may occur as a result of their high melting range and tendency to oxidize.<sup>(2)</sup>

Sintering is a method used to create objects from powders, its effects are based on diffusion of atoms, which takes place at elevated temperatures. During sintering, the atoms in powder particles diffuse across particle boundaries; this fuses the particles together to create a single solid piece.<sup>(1,2)</sup> DMLS employs a high-power laser source (a Ytterbium-Fibre-Laser with a nominal output of 200 W) that fuses alloy powder into a solid mass. The restoration is built up in layers, from the occlusal surface to the margins by scanning cross-sections from a 3D CAD file, that comprises the proposed restoration configuration, through the digitization of the selected abutment tooth or teeth. So, the step of definitive impression is not required. Moreover, porosity that are common with conventional casting is no more encountered, since up to 100% density can be achieved. Metal powders of titanium alloy or cobalt-chromium (Co-Cr) alloy are used by a commercial laser sintering

system EOSINT M (EOS, Munich, Germany).<sup>(1-8)</sup>

The bond strength of resin cements to dental restorations is essential, because of its influence on micro leakage, biologic complications, and survival<sup>(5)</sup>. Bonding between an alloy and a resin cement occurs through micromechanical and chemical retention phenomena. Increasing the roughness on the alloy surface provides the micromechanical retention, while a chemical reaction is believed to occur between the surface metal oxides and acidic functional monomers of the metal primers and/or resin cements. This allows the luting cement to penetrate and flow into such micro-retentions via increasing the metallic surface area available for bonding, in addition to increasing the surface energy of the treated surfaces. In this regard, sandblasting has been described to be beneficial.<sup>(9-12)</sup> Earlier studies reported that 4-Methacryloyloxyethyl trimellitic anhydride resins exhibit superior bonding to CoCr alloy, with different surface treatment methods.<sup>(13,14)</sup>

Generally, an oxide layer is readily available on the surface of base metal alloys. It has been concluded that the technique of alloy construction can affect the structure and thickness of this layer, which is essential for bonding. Hence, milled or laser sintered alloys may differ from cast alloys in their bonding characteristics to resin cements. Different surface treatments have been advocated to enhance bond strength of resin to metal alloys, such as sandblasting, tin plating, silica coating, with or without metal priming.<sup>(15,16)</sup> Few information are available on the bonding performance of adhesive luting agents to laser sintered Co-Cr alloy<sup>(17,18)</sup>. The objective of this in vitro study was to evaluate the shear bond strengths of resin cement bonded to 3D printed (laser sintered) Co-Cr alloy after different surface treatments. The null hypothesis was that tribochemical coating would contribute to higher shear bond strength of resin cement to laser sintered Co-Cr alloy as compared to alumina particles blasting.

## MATERIALS AND METHODS

A total of 30 disk shaped samples were constructed. A specially designed split Teflon mold was constructed (3mm in height and 8mm in diameter), within which, a self-cure composite (Concise, 3M, St Paul, Minn) was packed to produce disk shaped sample. Two glass slides were placed as base and top of the open end mold to ensure smoothness of the obtained disk. The disk was then, transferred for the construction of the laser sintered cobalt-chromium alloy disks. The composite disk was secured to a scanning peg with wax. The peg and disk were inserted into the Sirona inLab scanning chamber (Sirona InfiniDent Dental Systems GmbH, Germany), where they were scanned automatically. The inLab software recorded the data and displayed an exact 3D image of the disk on the monitor; the software then, automatically proposed a 3D design, the data was transmitted for fabrication on a specialized 3D RPMP. A special version of Co-Cr superalloy called EOS Cobalt Chrome SP2 powder (62-66%Co, 24-26%Cr, 5-7%Mo, 4-6%W and >1% Fe, Mn, Si) was used. The laser (nominal output of 200 W) immediately starts production layer upon layer. When fully fabricated, the finished disks were degassed for 5 minutes in a traditional furnace at 980°C. The oxide formed during the degassing process was removed using 250- $\mu$ m aluminous oxide. Disks were subjected to the high temperature treatment used in ceramic covering without deposition, then the disks were steam-cleaned. After simulated firings, each disk was secured within a copper holder with three screws to ensure a protruding surface of 1mm of the proposed fitting surface to be polished. The top of all disk specimens was subjected to metallographic grinding with a of silicon carbide abrasive papers (200–1000 grit size) under copious water rinsing in a grinding/polishing machine (Ecomet III; Buehler, Lake Bluff, IL, USA). The final polish was accomplished with diamond polishing compound with two different particle sizes. All disks were ultrasonically cleaned in a 70% alcohol bath for 3 min.

Disks were divided into three equal groups (n=10). The bonding surfaces were subjected to three surface treatments, Group A: blasting with 30 $\mu$ m grain size aluminum oxide, chemically modified with silicic acid, CoJet-Sand (ESPE, Seefeld, Germany) control group. Group B: sandblasted using 50 $\mu$ m aluminum oxide particles (Bego, Bremen, Germany) and Group C: sandblasting using 110 $\mu$ m aluminum oxide particles (Bego, Bremen, Germany). Sandblasting was performed vertically for 15 sec with 2 bar pressure using an intraoral sandblaster (Dento-Prep, Daugaard, Denmark) at 10mm distance from the blasting tip, simulating the treatment of the restoration' fitting surface<sup>(22)</sup>. Disks were ultrasonically cleaned in deionized water to remove any loose blasting particles and dried using absorbent paper. Custom-made teflon mold with an internal diameter of 5 mm and thickness of 2 mm was centered on the surface of the alloy specimens. Resin cement Super-bond C&B were applied within the mold after they were manipulated according to the manufacturer's recommendation. Super-Bond C&B is a self-cure adhesive resin cement that employs "4-META" (4-methacryloxyethyl trimellitic anhydride) as a diffusion promoter and "TBB" (tributylborane) as a polymerization initiator.

### Shear bond strength testing

Bonded assemblies were stored in an incubator at 37°C for 48hrs  $\pm$ 2hrs, then were subjected to 2000 thermal cycles between 5°C and 55°C, with a transfer time of 30 seconds and a dwell time of 30 seconds. After thermocycling, the specimens were stored at 37 degrees °C distilled water for an additional 48 hrs.

For shear testing, a material testing machine (Model LRX-plus Lloyd Instruments Ltd, Fareham; UK) with a load cell of 5kN using a specially constructed testing chisel. Shear bond strength was determined by shear mode of force, which

was applied at the alloy-resin cement interface at a crosshead speed of 1mm/min till debonding <sup>(15)</sup>.

Data were recorded using computer software (Nexygen-4.1; Lloyd Instruments). Loads were recorded in Newtons. The load at failure was divided by the bonding area to express the bond strength in MPa.

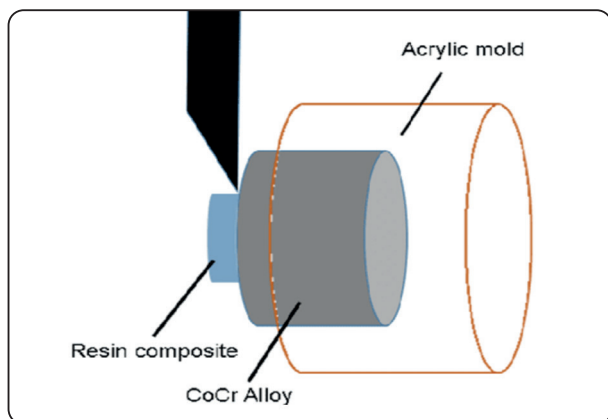


DIAGRAM (1): schematic presentation of the bonded assembly for shear testing

According to ANOVA results of shear bond strength measurements revealed a statistically significant difference between silica coating and alumina blasting (with different grits) However, no statistical significant difference was found between bond strength values obtained for 50 μm or 110 μm Al<sub>2</sub>O<sub>3</sub> sandblasted surfaces, as shown in Tables 1 and 2, and fig 1

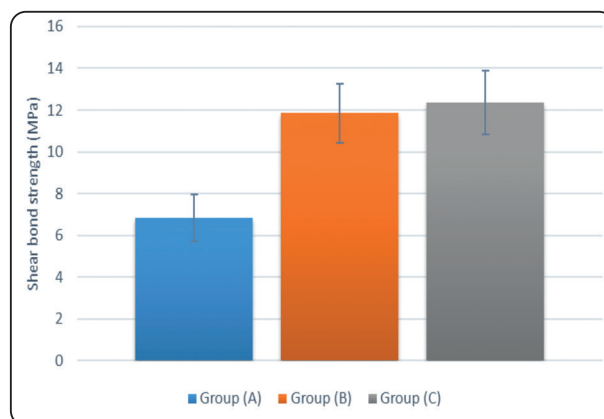


Fig. (1): Mean shear bond strength values of resin cement to laser-sintered Co-Cr alloy with different surface treatments

**Shear bond strength**

TABLE (1) Des: riptive statistics

Group	Mean	95% CI		SD	Minimumm	Maximum
		Lower	Upper			
Group (A)	6.84	6.00	7.69	1.14	5.11	7.94
Group (B)	11.85	10.80	12.89	1.41	10.21	14.40
Group (C)	12.35	11.22	13.48	1.53	10.12	14.21

**95% CI= 95% confidence interval for the mean; SD = standard deviation**

TABLE (2) Intergroup comparisons and summary statistics of shear bond strength values (MPa)

Shear bond strength			f-value	p-value
Group (A)	Group (B)	Group (C)		
6.84±1.14B	11.85±1.41A	12.35±1.53C	34.75	<0.001*

**Means with different superscript letters within the same horizontal row are significantly different, \*significant (p<0.05)**

## DISCUSSION

Alloy laser sintering became the topic of interest for researchers, for the manufacturing of dental metallic restorations. Most earlier studies on selective laser sintering have focused on Co–Cr dental alloys<sup>(1,2)</sup>. Some studies have focused on the evaluation of the marginal and/or internal fit of the restorations<sup>(6,10)</sup>, whereas others have tested the bond strength with dental porcelain<sup>(4,8,23)</sup>, internal porosity<sup>(24)</sup> and effect of surface treatments on micro-roughness<sup>(25)</sup>. However, their clinical behavior is still needed to be investigated. Differences in the manufacturing between conventional casting and laser sintering of a fine metallic powder can involve large differences in microstructural characteristics<sup>(26)</sup>. Few studies have been undertaken to evaluate this new technology as regard to bonding with dental cements. Therefore, the strength of resin cement bonded to laser sintered Co-Cr was evaluated.

In this study all samples were subjected to porcelain firing cycle to simulate laboratory procedures done for metal–ceramic restoration. Previous study showed variation in thickness of the oxide layer between laser-sintered and cast Co- Cr alloy while studying their bonding to porcelain<sup>(4)</sup>. They attributed their finding to variation in the percentage of oxides on the tested alloy surfaces, as influenced by manufacturing technique, which consequently, differentiate the interfacial characterization of metallic elements at the metal surface. On the other hand, Thermocycling was done to simulate oral condition where, thermal stress derived from the variation in thermal expansion coefficients between the resin and the metal can weaken the adhesive junction. This considered a useful method for pre-clinical assessment of bonding durability. According to earlier studies<sup>(12,14,17)</sup>, the effectiveness of the bond between dental cements and metal-ceramic restorations is critical for retention, as well as maintenance of a durable marginal seal and prevention of microleakage.

The resin cement used in this study, Super-Bond C&B was selected as it was verified that its component 4-META/MMA resin bonds to non-precious dental alloys (Ni-Cr alloy, Co-Cr alloy, as well as stainless steel). It is believed that bonding is due to the reactivity of 4-META with the surface layer of chromium oxide<sup>(27)</sup>. The selected adhesive cement was bonded to the sintered alloy without priming, as this might have influenced the obtained results.

Chemical reactivity is among the most important advantages of dental base-metal alloys, which enables them to bond directly to dental cements. To create a reliable bond between the metallic restoration and the adhesive resin, good wetting must take place and the stresses at the interface have to be minimum.<sup>(27)</sup> Silica coated (Group A) was selected as a control group due to its fine particle size (30  $\mu\text{m}$ ) making its abrasion rate to be much lower than conventional abrasives. Many investigators suggested that even fine crown edges can be treated via this technique with no damage.<sup>(18,19)</sup>

Among the conditioning methods applied, sandblasting with Cojets system showed a significantly lowest shear bond strength, as compared to the other tested groups. This finding can be partly attributed to the method of manufacturing. During laser sintering, the skin region of each powder particle was totally melt by the laser and underwent rapid solidification. This resulted in compact structures with small grain size<sup>(28)</sup>. As in the case of densely sintered ceramics, the higher density and lower porosity of sintered materials render them more resistant to chemico-mechanical treatments<sup>(29)</sup>. During sandblasting with Cojet sand, the force of impact causes the  $\text{Al}_2\text{O}_3$  to bounce back off the surface leaving a layer of silica behind, on the metal surfaces. However, this surface treatment method did not represent an advantage when applied to the alloy surface, since it did not increase the adhesive bonding of (group A), despite enriching the surface with silica. An explanation for this behavior may include the existence of poor chemical affinity between silica particles and cobalt



chromium alloys thereby, preventing complete wetting of the metal surface<sup>(29)</sup> or the presence of air pockets, which served to weaken the bond joint as claimed by other investigators<sup>(30,31)</sup>. In addition, other explanation could be related to the sandblasting pressure applied, or even to the low grit-size used.<sup>(29,32,33)</sup>

Air abrasion of alloy surfaces resulted in micro-roughening, through changing the surface texture. The large grit of aluminum oxide particles used in blasting might have affected surface topography<sup>(29,32)</sup>. Results of this study revealed a significant increase in shear bond strength of (group B & C) after alumina blasting, as compared to control group A, as shown in fig1. The shear bond strengths obtained from both grit sizes (50  $\mu\text{m}$  and 110  $\mu\text{m}$ ) was not significantly different indicating that their mechanical roughening effect positively enhanced the wettability of the surface, that is required to optimize the chemical integration between the alloy surface and cement layer thereby, providing high bond strength at the interface. This was in accordance with the former study by Eldemellawy M<sup>(34)</sup>, who found no statistically significant difference between the mean surface roughness values of laser sintered Co Cr alloy surfaces sandblasted with both 50 and 110  $\mu\text{m}$  aluminum oxide particles.

The insignificant mean value of shear bond strength between the two groups may be due to almost equal enrichment of their surface by Cr, and the mild variation in the percentage of alumina in between<sup>(35)</sup>.

Shear bond strength values after sandblasting with both grits of aluminum oxide (50 $\mu\text{m}$  and 110 $\mu\text{m}$ ) were in agreement with those in former reports<sup>(20,33,34)</sup>, where bond strengths obtained from both grit sizes were not significantly different for the tested alloys. On the other hand, the presence of reactive surface oxides, embedded aluminum and silicon as well as 4-META resin component partly account for the combined adhesive –cohesive mode of failure of the debonded samples.

## CONCLUSIONS

Within the limitations of the present study it was concluded that

1. Aluminum oxide blasting is considered the conventional, yet effective surface treatment method for laser sintered Co-Cr alloy to enhance resin-alloy bonding.
2. Silica coating as a surface treatment for laser sintered dental Co-Cr alloys should be re-evaluated.

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