



# Effect of Rare Light Earth Metal Lanthanum on Shear Bond Strength of Castable Cobalt Chromium Alloy to Porcelain- an in-Vitro Study

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Lanthanum, Cobalt-Chromium Alloys, Shear Bond Strength, Porcelain, Dental Prosthetics, Lost Wax Technique, Induction Casting, Grain Growth, Grain Refining

## ABSTRACT:

**Introduction:** Metal-ceramic (PFM) restorations, particularly base metal alloys, are widely used in dentistry. While nickel-chromium and cobalt-chromium (Co-Cr) alloys offer high adhesion, nickel-chromium presents stability issues and potential allergic reactions, making Co-Cr alloys preferable due to their mechanical strength, biocompatibility, and affordability. However, thermal incompatibility with porcelain leads to fractures, reducing durability. Advanced techniques are costly and inaccessible in many regions, necessitating traditional methods like induction and lost-wax. This study examines the influence of lanthanum (La), a rare earth metal, on the shear bond strength of castable Co-Cr alloys with porcelain.

**Materials and Methods:** Ninety cylindrical inlay wax patterns (5 mm × 15 mm) were divided into three groups: Group A (0% La), Group B (0.03% La to be added), and Group C (0.06% La to be added). The samples were cast, finished, sandblasted, and ultrasonically cleaned. Ceramic sintering was done layer by layer till dimensions of 5 mm × 5 mm achieved. Shear bond strength tests were conducted using an Instron universal testing machine. Statistical analyses were performed using SPSS version 29.0, with significance value  $p < 0.05$ .

**Results:** The addition of lanthanum notably improved the mean shear bond strength. Group C exhibited the highest bond strength (54.44 MPa), followed by Group B (36.19 MPa) and Group A (25.47 MPa). Multiple comparisons using the Student's t-test further affirmed the statistical significance of differences between the test groups. Consistently low p-values ( $<0.05$ ) emphasized the presence of meaningful distinctions in bond strength attributable to La incorporation. The presence of lanthanum reduced adhesive failures and increased cohesive failures, indicating an enhanced bond interface as seen in stereomicroscopic examination.

**Conclusion:** This study examines at how lanthanum (La) inclusion influences the shear bond strength of Co-Cr alloys and porcelain. The results reveal that La increases bond strength, with focus having an important impact. A comparison of alloys containing 0%, 0.03%, and 0.06% La demonstrated increased adhesion due to oxide layer alteration, greater wettability, and a stronger metal-ceramic contact. Failure mode research revealed a transition from adhesive to cohesive failure, implying a stronger relationship. The study determined the ideal La concentration for maximal strength, providing insights into high-performance Co-Cr alloys for dentistry and biomedical applications.

## Introduction

Metal-ceramic restorations are widely utilized in dentistry due to their excellent mechanical properties

and acceptable aesthetics.<sup>1-4</sup> These restorations typically use modern dental casting alloys, including noble-metal alloys like Au-Pt and base-metal alloys such as Ni-Cr



and Co-Cr.<sup>5</sup> Noble-metal alloys are particularly advantageous because of their superior corrosion resistance in oral environments, high elongation, and excellent biocompatibility.<sup>6-7</sup> However, the high cost and limited availability of precious metals restrict their broader application in dental practice.<sup>8-11</sup> In this context, Co-Cr alloys have emerged as economical and effective alternatives for dental restorations. Base-metal alloys like Co-Cr provide favourable mechanical properties, including high strength and lower density compared to noble-metal counterparts.<sup>12-13</sup> Additionally, concerns over the allergenic potential of nickel and the toxicity of beryllium have further established Co-Cr alloys as preferred dental biomaterials over Ni-Cr alloys.<sup>14-17</sup> Co-Cr alloys exhibit excellent biocompatibility,<sup>18</sup> superior marginal integrity,<sup>19</sup> high mechanical strength during ceramic firing, and a high modulus of elasticity.<sup>20-21</sup> These characteristics, combined with affordability, make Co-Cr alloys a suitable choice for fixed prosthesis frameworks.<sup>22-24</sup> The clinical success and longevity of metal-ceramic restorations are heavily influenced by the strength of the bond between the metal and the ceramic. Despite extensive efforts to optimize this bond, issues such as ceramic fractures and debonding remain significant challenges.<sup>25</sup> Castable Co-Cr alloys have thermal compatibility with porcelain due to martensitic transformations during porcelain firing. These transformations cause volumetric expansion and residual stresses that weaken the bond and increase the likelihood of ceramic fractures or debonding.<sup>26-27</sup> Although various methods have been explored to enhance metal-ceramic bonding, limited research exists on the incorporation of rare earth elements into dental casting alloys. Lanthanum (La), a rare light earth metal with a high melting point and excellent corrosion resistance, has shown promise in improving the mechanical properties and biocompatibility of Co-Cr alloys.<sup>28</sup> Previous research suggests that small amounts of lanthanum do not pose toxic risks to human health.<sup>29-30</sup> This study investigates the effect of lanthanum addition on the shear bond strength between castable Co-Cr alloys and porcelain. Using shear bond tests, this study evaluates Co-Cr alloys with varying concentrations of lanthanum, hypothesizing no significant differences in bond strength among the groups. The findings aim to provide valuable insights into the potential of lanthanum as an additive for

enhancing the durability and clinical performance of Co-Cr-based dental prostheses.

## Materials and Methods

Ninety cylindrical wax patterns (5 mm diameter, 15 mm height) were fabricated using Green Stick medium inlay wax (GC Corporation, Tokyo, Japan) and verified for dimensions with a digital Vernier calliper (Cobra Metal Productions, Ontario, Canada). The patterns were randomly assigned into three groups, with 30 samples in each:

**Group A:** Control (no lanthanum will be added)

**Group B:** 0.03% lanthanum by weight will be added

**Group C:** 0.07% lanthanum by weight will be added

Lanthanum content was calculated using the following formula:

$$\text{Percentage of weight} = \left( \frac{\text{Desired Weight}}{\text{Total Weight}} \right) \times 100$$

Wax sprues (Bego Canada Inc.) were attached to the centre of each pattern using PKT instruments (API Germany). The patterns were mounted onto crucible formers with inlay wax, and phosphate-bonded investment material was mixed, poured, and allowed to set. After the investment material had set, the patterns were subjected to burnout at 900°C to remove the wax. Casting was performed using an induction casting machine (Ducatron Series 3; UginDentaire, Seyssins, France) with Co-Cr alloy (Adentatec Ltd, Germany). Lanthanum microparticles were added to the molten alloy during casting. The molten metal was injected into the casting ring using centrifugal force. After cooling, the castings were retrieved, ultrasonic cleaned in distilled water (Vitasonic II; VITA Zahnfabrik, Germany). The ceramic build-up was performed by layering opaque and dentine ceramics (VITA VMK 95, VITA Zahnfabrik Germany) using a ceramic furnace (Vacumat40, VITAZahnfabrik Germany). The opaque porcelain was applied in thin layers, dried, and sintered. Dentine porcelain was then applied using sable brushes and a custom mould for condensation, followed by cleaning and sintering. Enamel buildup was completed and sintered, and the final layer was polished with a ceramic polishing kit. A thin glaze layer was applied and sintered as per the manufacturer's instructions. The shear bond strength of the metal-ceramic samples was



evaluated using a universal testing machine (Instron) at a crosshead speed of 0.5 mm/min with a 200 kN load. Data were analyzed using one-way ANOVA, and additional statistical analysis was conducted with descriptive statistics and chi-square tests (SPSS version 29.0). After testing, the samples were examined under 80× magnification using a stereo microscope (Magnus Opto Systems, India) to classify the fractures as adhesive, cohesive, or mixed.

**Results**

This study aimed to investigate the effect of varying lanthanum (La) concentrations on the bond strength of cobalt-chromium alloys used in dental prosthetics. The analysis revealed that the bond strength increased with the incorporation of La. Group C exhibited the highest mean bond strength of 54.44 MPa, followed by Group B with 36.19 MPa, and Group A, the control group, with 25.47 MPa. The standard deviation values indicated variability within each group, with Group C demonstrating the most consistent bond strength values (Table I).

**Table I- Multiple comparison between all the three groups using student T- test**

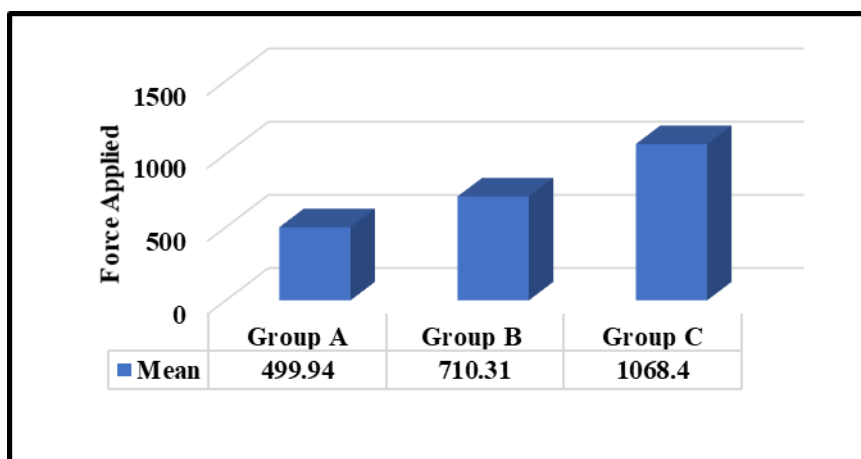
Pair	Mean difference	SD	SE	95% Confidence Interval		t	df	P value	
				Upper	Lower				
Group 1	Group 2	-10.71	3.5	0.6	-12	-9.42	-16.9	29	0
	Group 3	-28.96	7.1	1.3	-31.6	-26.3	-22.3	29	0
Group 2	Group 3	-18.24	6.9	1.3	-20.8	-15.66	-14.4	29	0

Group C exhibited the highest mean force of 1068.40 N, indicating that greater force was necessary to achieve bond failure (Table II and Graph I). This reinforces the

idea that La incorporation results in stronger, more durable bonds between the metal and ceramic.

**Table II- Mean of different between the forces applied on different test groups**

S.No.	Groups	Minimum	Maximum	Mean	SD
1	Group A	426.84	601.31	499.94	47.98
2	Group B	639.38	798.93	710.31	47.08
3	Group C	901.18	1373.16	1068.40	118.60



**Graph I- Mean differences between the forces applied on different test groups**



One-way analysis of variance (ANOVA) revealed statistically significant differences between the groups, although the p-values exceeded the conventional significance threshold of 0.05 (Table III). However, a more pronounced trend was observed between Groups A and B, suggesting a notable difference in bond strength between the control and the lowest La concentration. This indicates that while the differences between other pairs did not meet conventional significance criteria, there is still a meaningful trend in the data.

**Table III- One way ANOVA results for ultimate bond strength**

Groups		Sum of Squares	df	Mean Square	F	Sig.
Group A & Group B	Between Groups	158.73	27	5.87	1.43	0.5
	Within Groups	8.188	2	4.09		
	Total	166.92	29			
Group A & Group C	Between Groups	154.74	26	5.95	0.96	0.6
	Within Groups	18.643	3	6.21		
	Total	173.39	29			
Group B & Group C	Between Groups	146.08	26	5.61	0.81	0.7
	Within Groups	20.84	3	6.94		
	Total	166.92	29			

Further statistical analysis with Student's t-test confirmed significant differences in bond strength between the groups, with consistently low p-values ( $<0.05$ ) indicating a strong correlation between La incorporation and bond strength enhancement (Table I). Stereo microscope examination of failure modes revealed notable differences across the groups. In Group

A, 80% of failures were adhesive, with 20% classified as mixed fractures. Group B 30% mixed failures, 10% cohesive failures, and 60% adhesive failures. In contrast, Group C displayed 20% adhesive failures, 20% mixed failures, and 60% cohesive failures, indicating a shift towards cohesive failures as La concentration increased. (Picture I)



**Figure I: Stereomicroscope images at 80x magnifications revealing different types fractures 1a Adhesive fracture between metal ceramic, 1b Mixed type of fracture between metal ceramic and 1d showing Cohesive type fracture**

The consistent findings across bond strength, applied force, and failure modes support the rejection of the null hypothesis. The increase in bond strength and the shift

in failure modes with higher La content indicate that La incorporation could have practical applications in



improving the durability and reliability of dental prosthetics.

## Discussion

Cobalt-chromium (Co-Cr) alloys are known for strength, biocompatibility, and corrosion resistance, while porcelain offers a natural look. Lanthanum, a rare earth element, enhances dental restorations by improving the bond between metal and porcelain through the formation of lanthanum oxide. This results in more durable and cost-effective dental restorations.<sup>28</sup>

Oxidation is a critical process in preparing the metal substructure for porcelain bonding. Post-finishing, metal-ceramic castings are cleaned and subjected to heat treatment (oxidation) in a porcelain furnace, either in air or vacuum, at specific temperatures for set durations. However, a universal oxidation protocol does not exist for all alloys due to differences in the high noble, noble, and base metal-ceramic alloys concerning atmosphere type, temperature, and duration settings. Moreover, oxide composition varies due to minor alloying elements. Noble ceramic alloys generally include oxidizable trace elements to form an adherent oxide layer, while base metal alloys rely on trace elements for forming a specific oxide layer essential for stable bonding. Uncontrolled oxidation in base metal alloys may result in over-oxidation, leading to thick, non-adherent oxides and eventual bond failures with porcelain.<sup>31</sup>

Adding lanthanum (La) to Co-Cr alloys significantly enhances their chemical affinity for oxygen, facilitating reactions with oxides, particularly during high-temperature porcelain firing. This addition promotes the formation of  $\text{La}_2\text{O}_3$  and  $\text{Cr}_2\text{O}_3$  as primary oxide layer components. Notably,  $\text{La}_2\text{O}_3$  differs from  $\text{Cr}_2\text{O}_3$  by having a higher number of ion channels, leading to thicker reaction diffusion oxide layers. Consequently, this strengthens chemical bonds. Under specific conditions, lanthanum oxides may penetrate the metal matrix, further boosting mechanical bonding.<sup>28</sup> Traditional casting or the lost wax technique is one of the oldest and most economical methods for fabricating dental prostheses. Despite advancements in manufacturing techniques, which show comparable performance in porcelain adhesion and surface hardness, the bond strength of restorations remains largely unaffected by the method used.<sup>32, 33, 4</sup> In this

study, economical lost wax and induction casting were employed due to their affordability and precision in producing detailed castings. In the lost wax technique, molten metal cools in a clean container, with alloy particles solidifying first as the temperature falls below the liquidus. These particles act as nuclei for further solidification, known as nucleation. As cooling progresses, the nuclei form crystals or "grains," which grow as atoms bond through metallic bonds. The process ends with grains meeting at boundaries, forming a solid structure comprising randomly arranged crystals.<sup>34</sup> Solid structures are inherently more stable than liquid phases due to their lower energy levels. As molten metal transitions to a solid state, energy is released, referred to as the latent heat of solidification, which is equivalent to the heat of fusion. Nucleation occurs rapidly during the cooling of molten metal, forming clusters of atoms known as nuclei or embryos. This process can occur through homogeneous or heterogeneous mechanisms. Homogeneous nucleation involves rapid formation of a solid structure without the inclusion of external particles, resulting in irregular polycrystalline grains. Conversely, heterogeneous nucleation involves the introduction of external solid particles, such as high melting point elements like iridium, which promote uniform nucleation and reduce grain size.<sup>35,36</sup> Grain refiners, such as iridium, are high melting point metals added to alloys to remain solid while the surrounding material is molten. These particles act as nucleation sites, enhancing physical properties like ductility and tensile strength. The solidification process significantly influences metal properties, as atomic diffusion from molten metal to nuclei forms crystals. These crystals are characterized by irregular arrangements, structural discontinuities, and imperfections instead of a uniform orientation. The crystallization process often results in dendritic morphology, which resembles branched trees. Dendrites, elongated crystals, exhibit growth driven by thermal supercooling mechanisms. During this process, extensions or elevated areas emerge at the metal's solidifying front, advancing into regions of negative temperature gradients. In clinical applications, base metal dental alloys solidify with dendritic microstructures, while noble metal alloys achieve equiaxed polycrystalline structures through grain-refining elements like indium, ruthenium, or rhenium.<sup>24, 37</sup> The durability of metal-ceramic restorations depends



on reliable bonding between the metal and ceramic layers, primarily facilitated by the oxide layer. If the oxide layer is absent or too thin, it may be eliminated during ceramic sintering, resulting in weak bonding. However, overly thick oxide layers can also cause issues due to poor cohesive strength. The composition of the metal oxides formed during oxidation is influenced by the alloy's composition and surface treatment.<sup>38</sup> Uniform microstructures promote homogeneity within the oxide layer, ensuring better continuity and enhancing the corrosion resistance of Co-Cr alloys. Lanthanum oxides, when integrated into the native oxide layer, significantly alter its properties, improving bond performance. Moreover, lanthanum oxides reduce interfacial energy, enhancing wettability between the metal and the oxide layer.<sup>28</sup> Lanthanum also interacts readily with oxides such as  $\text{Cr}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$ , altering the permeability of the oxide layer. This change facilitates easier atomic diffusion, promoting chemical bonding between the metal and ceramic. Simultaneously, lanthanum enhances oxidation resistance at high temperatures. Lanthanum oxides embedded at the interface penetrate the metal matrix, reinforcing the mechanical bond between the oxide layer and the matrix.<sup>26,28</sup> During diffusion, metal cations move outward while oxygen ions migrate inward, potentially creating vacancies in the metal matrix and weakening bond strength. However, lanthanum mitigates this outward diffusion, reducing vacancy formation and maintaining bond strength. Chromium, particularly  $\text{Cr}_2\text{O}_3$ , dominates the oxide layer due to its lower standard free energy for reaction with oxygen compared to elements like Co, Si, Mo, W, and Ti. This typically limits the thickness of the diffusion layer.<sup>39</sup> However, lanthanum's strong affinity for oxygen promotes the formation of  $\text{La}_2\text{O}_3$  and  $\text{Cr}_2\text{O}_3$  as primary oxide layer components. These components, characterized by numerous ion channels, substantially increase the reaction diffusion and oxide layer thickness while improving chemical bond strength.<sup>28</sup> Under certain conditions, lanthanum oxides may penetrate the metal matrix, further enhancing mechanical bond strength via improved chemical interactions. Previous studies by Bae et al. (2015) report the bond strength of castable Co-Cr alloy to range between 38.44 MPa and 41.40 MPa.<sup>40</sup> Additionally, the shear bond strength of laser-sintered cobalt-chromium is 34.56 MPa, exceeded that of cast nickel-chromium which is 23.88 MPa and

cast cobalt-chromium is 23.70 MPa, which had the lowest strength among the three.<sup>41</sup> In this study, the highest mean bond strength was recorded at 54.44 MPa, followed by Group B at 36.19 MPa and Group A at 25.47 MPa. The standard deviation provides insight into bond strength variability within each group. A stereomicroscope was used to analyse the fractured surfaces of samples, classifying fractures as adhesive, cohesive, or mixed.<sup>42</sup> The analysis revealed significant differences in failure proportions among groups. Group A exhibited 80% adhesive failures, Group B showed 60% adhesive failure, Group C experienced 15% adhesive failures, and 73% cohesive failures. The high proportion of cohesive failures in Group C indicates the oxide layer's greater strength compared to the ceramic material. Co-Cr alloys enhanced with lanthanum have demonstrated substantial improvements in bonding mechanisms and bond strength.

## Conclusion

The study conclusively demonstrated that the addition of La to cobalt chromium alloys significantly enhances metal-ceramic bond strength. The consistent findings across bond strength, applied force, and failure types support the rejection of the null hypothesis. The increase in bond strength and change in failure modes with higher La content suggests practical applications in improving the durability and reliability of dental prosthetics.

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