



Metal-ceramic bond strength of a cobalt chromium alloy for dental prosthetic restorations with a porous structure using metal 3D printing

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ABSTRACT

Selective laser sintering (SLS) is a new type of additive material manufacturing technology. The development of precise 3D metal printing technology has enabled the printing of complicated metal structures, particularly in the medical field. Finding a way to integrate new technologies with Co–Cr alloys for the precision manufacturing of dental restoration materials and a way to improve the metal-ceramic bonding strength of the materials have become a key focus of dental restoration clinical trials. The purpose of this study is to evaluate bonding strength and ceramic adhesion between metal and ceramics using Co–Cr specimens with different porous structures manufactured using SLS technology. According to the international standard ISO9693:1999, we printed three sets of 10 rectangular Co–Cr alloy test specimens of the same size ($25 \times 3 \times 0.5$ mm) using an SLS-3D metal printer and fused a ceramic layer ($8 \times 3 \times 1.1$ mm) to the center of the Co–Cr alloy test specimen. Before testing, we conducted stress and fracture simulation analysis on three specimen types (no holes, circular-shaped holes, and rhombic-shaped holes), using ABAQUS results to predict the results of three-point bending tests. These simulation results were then compared with the experimental data. We used three-point bending tests to assess the bonding strength of the fabricated metal-ceramic bonding surface. We also used a digital microscope ($100 \times$ and $200 \times$) to observe the surface conditions of the samples. Finally, we analyzed the results using one-way analysis of variance. The ABAQUS bending simulations indicated that the bending energy decreased sequentially for the hole-free, circular-hole and rhombic-hole specimens. Similarly, when the three types of test specimen were manufactured using SLS, significant differences in bending energy were observed between the rhombic-hole specimens and both the hole-free ($P < 0.05$) and circular-hole specimens ($P < 0.05$). In addition, the bond strength for all groups was higher than the international minimum standard of 25 MPa (33.36 ± 3.17 MPa). In this research, the bond strength of all three metal-ceramic test specimens was higher than the international minimum standard of 25 MPa set by ISO1999/9693. However, the circular porous design did not show previous diversity with other porous shape design. In addition, due to limitations in the accuracy of 3D printing using SLS, the structural advantages our proposed specimen design are difficult to verify. Therefore, we plan to develop new structural designs to improve the bonding strength of metal-ceramic structures in future work.

1. Introduction

Additive manufacturing (AM), which is generally known as 3D printing (3DP) or rapid prototyping (RP), was first introduced in the late 1980s [1–3]. Since then, 3DP technology [4] has been used to produce accurate one-off, complex 3D geometrical structures from digital data using a variety of materials. Compared with conventional manufacturing methods, this technology is particularly useful for dentistry applications, particularly considering the advances that have been made in 3D imaging and modelling technologies. As such, 3DP has been used to overcome limitations inherent to the processing of materials for various applications.

Over the past few years, 3DP technology has developed rapidly. Due to the recent advances in multi-material printing methods, selective laser sintering (SLS) [5,6] technology is now able to handle a wide range of materials (such as wax, cermet, ceramics, and metal-polymers) for the creation of solid structures, in which a laser is aimed automatically at points in space defined by a 3DP model. The SLS method [7] allows parts to be fabricated without requiring any part-specific tools, meanwhile, it also can shorten the design and production cycle, and promises to revolutionize traditional manufacturing processes by significantly reducing time and costs.

The ability to produce high-quality AM products illustrates that SLS with 3DP offers significant technical advantages compared with

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traditional casting and CAD/CAM techniques in the manufacture of dental restorations [8–10]. As a consequence, the development provides a new direction for the establishment of medical models and progress in clinical trials in dental medicine. Porcelain-fused-to-metal (PFM) [11–13], which is used to provide strength to a crown or bridge, has a translucency that mimics natural tooth enamel, a characteristic that is particularly desirable. Because metals possess excellent compressive strength and high fatigue resistance, porous metallic scaffolds made of titanium (Ti) and tantalum (Ta) and biocompatible alloys such as Co–Cr alloys have been proposed as teeth replacement materials. These restorations are very strong, durable, and resistant to wear because the combination of porcelain and metal creates a stronger restoration than porcelain alone.

The improvement in the precision of metal printing has led to advantages for computerized dentistry. However, in stomatology, dental restoration is a precision technology that requires not only post-processing but also a higher printing precision than in other fields. Repairing teeth is still expensive and time-consuming because the cermet frequently fractures after teeth restoration. Therefore, in order to prolong the life of a porcelain-fused-metal (PFM) crown, sufficient bonding strength between the metal substrate and the porcelain veneer is crucial.

In this respect, SLS printing still struggles to accurately print complex and highly developed architectural structures, such as complex hive structures, due to the porous surface of metal alloys [14,15]. In response to this, dental researchers have developed a method of sealing the porous surface by applying a coating to increase the bond strength between the Co–Cr alloy substrate and the overlying porcelain [16–18]. However, little relevant data regarding the success of this approach is available for different types of Co–Cr alloy substrate manufactured using SLS printing technology.

Therefore, the goal of this study is to evaluate whether the nature of the porous structure of the metal substrate has a positive effect on the bond strength between it and the ceramic layer. We use SLS with 3DP to manufacture Co–Cr alloy substrates with different porous structures to determine the effect of these structures in dental restorations. We also employ computer simulations to predict the bonding strength of our designed porous structures with the ceramic layer using ABAQUS software.

2. Materials & methods

We first designed three types of Co–Cr alloy porous specimen (hole-free, circular-hole, and rhombic-hole specimens) and fabricated 30 samples (10 samples per type for a total of 30) in a stereolithography (STL) file using Solidworks® software (Fig. 1). We then used ABAQUS to simulate the bonding strength of the three specimen types with the ceramic layer. In the three-point bending simulations, we set the distance from the probe head to the plate top surface at 1 mm. The loading force was 1.5 mm/min according to ISO Standard 9693:1999. Two boundary conditions were applied to our model: one fixing the bottom two supports to be rigid and immovable (Fig. 1b; the bottom two white supports), and one fixing the upper support to apply the load force (Fig. 1b; the upper white support). The mesh size of the Co–Cr alloy substrate and the ceramic layer was 0.1 and 0.2, respectively, and the mesh type was an eight-node, quadratic tetrahedral solid (ABAQUS element type C3D8R). The properties of the components are shown in Table 1.

For the simulations, we used an SLS device (EOSINT M270; EOS GmbH, Munich, Germany [19]) to manipulate the Co–Cr alloy powder at a scan speed of 7 m/s, a laminate thickness of 100 μm , a YW fiber of 200 W, a manufacturing speed of 20 m^3/s , a laser spot size of 0.1 mm and a particle size of 20 μm . These specifications were in accordance with the manufacturer's recommended standards. The composition of the metal powder is shown in Table 2. Sandblasting was then carried out for the SLS group specimens. At a pressure of 0.4 bar, the finished

alloy sample was abraded with 50- μm alumina oxide particles (Cobra, Renfert GmbH, Hilzingen, Germany) in the air. To assess the surface of the alloy sample, random samples were extracted and observed with a digital microscope (Olympus Microscope BH41).

Samples of the same size were then fabricated using a two-step process. First, using the company's manufacturing method, porcelain powder (8.0 mm long, 3.0 mm wide, and 0.5 mm high) was sintered onto the Co–Cr alloy substrate (25.0 mm long, 3.0 mm wide, and 0.5 mm high), and any excess porcelain was removed. The second step involved measuring and rebuilding the tiles after firing if an additional finish was required. This process was then repeated until the sample reached the desired size.

Finally, three-point bending tests were performed using a universal testing machine (Oriental TM OTU-2, Oriental TM Corp., Gyeonggi-do, Korea) with a crosshead speed of 1.5 mm/min to measure the metal-ceramic bonding strength of each group. In order to analyze the bond strength between the metal and the ceramic layer, we used a one-way analysis of variance (ANOVA) to evaluate the differences between the three specimen designs. The results for each group were tested based on $\alpha = 0.05$ (SPSS 20.0; SPSS Inc., Chicago, IL, USA).

3. Results and discussion

In the present research, we used SLS printing technology with a Co–Cr metal alloy to print three different structures (hole-free, circular-hole, and rhombic-hole specimens) and evaluate the bonding force between these specimens and a ceramic layer. Unlike the simulation results, the experimentally obtained bonding strength indicated that the metal-ceramic combination has no obvious advantages over other combination types using most conventional processes [20,21]. However, for SLS metal printing, the structural design and the optimization process revealed that the rhombic-hole specimens had the largest void ratio and thus the lowest bending strength (28.98 ± 3.48) of the three designs.

The bending energy of the hole-free, circular-hole, and rhombic-hole specimens decreased in order, which is consistent with the simulation results. From the experiment, the bonding strength between the metal and the ceramic layers of the three groups of test samples was measured separately. The bonding strength of the hole-free, circular-hole, and rhombic-hole specimens was 32.52 ± 3.36 MPa, 32.49 ± 2.38 MPa, and 28.98 ± 3.48 MPa, respectively (Table 3). Statistically significant differences were found between the three specimen groups ($F = 4.268$; $P = 0.025$, Table 4). Least significant difference (LSD) tests demonstrated statistically significant differences between the rhombic-hole group and both the hole-free ($P < 0.05$) and the circular-hole groups ($P < 0.05$), but no difference was found between the hole-free groups and the circular-hole groups ($P > 0.05$; Table 5). As observed by digital microscope (Fig. 2), the surface of real SLS-manufactured samples was very rough and had numerous gaps, indicating that the circular-hole and rhombic-hole specimens were not printed perfectly by the 3D printer. In addition, Fig. 3 indicates that the porcelain was not perfectly integrated with the Co–Cr alloy substrate in the fabrication of the circular-hole and rhombic-hole specimens using 3DP, which can be considered a manufacturing error. We randomly selected a substrate sample from each group and observed the metal surface using a digital microscope, finding a slight difference in the width interval between the test specimens (Fig. 4), which can be attributed to the traces produced during SLS printing. It has been observed in several previous SLS studies with metals and ceramics that the in-situ heating of the powder bed alleviated many of the problems associated with SLS processing, such as wettability and thermal distortion [22,23]. Direct metal SLS, which is a typical RP technique, is generally carried out line-by-line, meaning that the balling effect may result in the formation of discontinuous scan tracks. Balling also tends to increase porosity and can even lead to delamination induced by poor inter-layer bonding in combination with thermal stress. Therefore, the

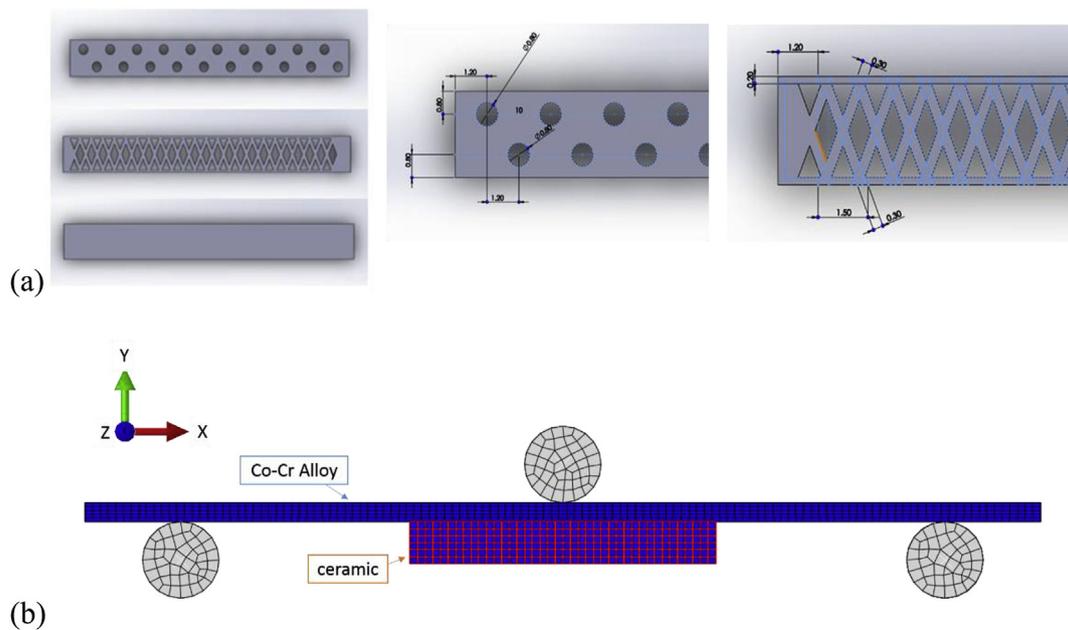


Fig. 1. (a) Three Co-Cr alloy samples were designed using Solidworks® software. From top to bottom: circular holes, rhombic holes, and no holes. (b) Prophase simulation used the three-point bending test in ABAQUS.

Table 1
Simulation settings for ABAQUS.

Materials	E (MPa)	Poisson's ratio (ν)
Co-Cr Alloy [32,33]	198.0	0.33
Ceramic VITA VM13 [33]	91.0	0.28

balling effect associated with laser-sintered powder severely degrades SLS quality. This phenomenon can also lead to poor stress distribution within the samples [24]. Nan Xiang et al. [25] conducted research with Co-Cr alloys and found that a bonding strength of 44 ± 5 MPa, which is slightly higher than the bonding strength observed in the present study. In addition, in our study, there was no obvious trend between our designed porous structures. This discrepancy may be due to a number of factors. First, it may be due to the manufacturing process used to cast the ceramic powder onto the Co-Cr substrate. As suggested earlier, the sintering bed temperature, laser power speed, and presence of impurities in the alloy may be influential during the sample fabrication process. For example, Oh et al. sintered spherical unalloyed titanium powder with and without applied pressure and achieved a porosity range of 5–37% [26]. Young's modulus and compressive yield strength decreased linearly with increasing porosity, and at 30% porosity, the stiffness of the porous titanium was close to that of human cortical bone (20 GPa). Therefore, any sintering operation used to fabricate alloy implants requires a non-oxidizing environment to achieve a suitable bonding strength.

Secondly, the discrepancy between Nan Xiang et al.'s [25,27] results and our own may be due to differences in the 3DP method, i.e., between selective laser melting (SLM) and SLS printing. Sorin Porojan et al. [28] calculated the surface roughness of specimens produced using SLS and SLM, showing that the roughness of the specimens produced with SLM method was considerably higher than that for SLS-derived specimens,

Table 2
Material composition (wt%).

	Co	Cr	W	Nb	V	Mo	Si	Fe	Mn
SP2	61.8–65.8	23.7–25.7	4.9–5.9	–	–	4.6–5.6	0.8–1.2	max 0.5	max 0.1

Table 3
Descriptive statistics for the bond strength (MPa) of the metal-ceramic specimens.

Group	N	Mean ± SD	Max	Min	Range (Max-Min)
Hole-free	10	32.52 ± 3.36	37.46	27.48	9.97
Circular holes	10	32.49 ± 2.38	35.57	28.22	7.35
Rhombic holes	10	28.98 ± 3.48	35.87	24.31	11.56

Table 4
Results for one-way ANOVA.

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	82.633	2	41.316	4.268	.025
Within Groups	261.350	27	9.680		
Total	343.983	29			

Table 5
Multiple comparisons for one-way ANOVA.

(I) term	(J) term	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
none	circular	.02226	1.39138	.987	–2.8326	2.8771
	rhombic	3.53171 ^a	1.39138	.017	.6768	6.3866
circular	none	-.02226	1.39138	.987	–2.8771	2.8326
	rhombic	3.50946 ^a	1.39138	.018	.6546	6.3643
rhombic	none	–3.53171 ^a	1.39138	.017	–6.3866	–.6768
	circular	–3.50946 ^a	1.39138	.018	–6.3643	–.6546

^a Mean difference is significant at the 0.05 level.

technique with 3DP manufacturing still has a few limitations related to its process parameters (e.g., processing atmosphere, laser processing settings, layer thickness, and the type of laser employed for the sintering process) and material properties (e.g., powder particle size, shape, and distribution).

4. Conclusion

In this research, three types of metal-ceramic specimen with different structures were fabricated using SLS, and it was found that the bond strengths of the three designs were all higher than the international minimum standard of 25 MPa set by ISO1999/9693. Therefore, these designs can be applied to teeth restoration. The roughness of the specimens produced with SLM method was considerably higher than that for SLS-derived specimens, resulting in a higher bonding strength for SLM over SLS. And then that pores or defects on the surface can increase the bonding strength of ceramics. With the further development of AM technology, printing accuracy will increase and enable specimens that are identical to the designed structure to be fabricated, which can be helpful in the development of dental prosthodontics.

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