http://jap.or.kr | J Adv Prosthodont 2015;7:312-6 | http://dx.doi.org/10.4047/jap.2015.7.4.312

In vitro evaluation of the bond strength between various ceramics and cobalt-chromium alloy fabricated by selective laser sintering

Eun-Jeong Bae, Hae-Young Kim, Woong-Chul Kim, Ji-Hwan Kim*
Department of Dental Laboratory Science and Engineering, Korea University, Seoul, Republic of Korea

PURPOSE. This study aimed to present the clinical applicability of restorations fabricated by a new method, by comparing the bond strength of between ceramic powder with different coefficient of thermal expansion and alloys fabricated by Selective laser sintering (SLS). **MATERIALS AND METHODS.** Fifty Co-Cr alloy specimens (25.0 × 3.0 × 0.5 mm) were prepared by SLS and fired with the ceramic (8.0 × 3.0 × 0.5 mm) (ISO 9693:1999). For comparison, ceramics with different coefficient of thermal expansion were used. The bond strength was measured by three-point bending testing and surfaces were observed with FE-SEM. Results were analyzed with a one-way ANOVA (α=.05). **RESULTS.** The mean values of Duceram Kiss (61.18 ± 6.86 MPa), Vita VM13 (60.30 ± 7.14 MPa), Ceramco 3 (58.87 ± 5.33 MPa), Noritake EX-3 (55.86 ± 7.53 MPa), and Vintage MP (55.15 ± 7.53 MPa) were found. No significant difference was observed between the bond strengths of the various metal-ceramics. The surfaces of the specimens possessed minute gaps between the additive manufactured layers. **CONCLUSION.** All the five powders have bond strengths higher than the required 25 MPa minimum (ISO 9693); therefore, various powders can be applied to metal structures fabricated by SLS. ***[J Adv Prosthodont 2015;7:312-6]***

KEY WORDS: Rapid prototyping; Selective Laser Sintering; Dental technique; Bond strength; Coefficient of thermal expansion

INTRODUCTION

Recent advances in dental equipment allow restorations to be fabricated using a variety of computer-aided technologies. This equipment is advantageous because it shortens work time by reducing manual processing and enables the mass-production of highly precise prostheses.[1] Within the field of dental restoration, the use of computer-aided technology can be divided into two primary categories: computer aided design/computer aided milling (CAD/CAM) and additive manufacturing. Within the CAD/CAM approach, a CAD is generated and used as a virtual template to cut/mill a reconstruction from solid blocks of predefined dimensions.[2] Alternatively, one of the attractive features of selective laser sintering (SLS) is that materials are not wasted, unlike in milling, because only the shape of the reconstruction designed by CAD is additively manufactured.[3]

SLS[4,5] is the most popular method in dentistry for additive manufacturing using Co-Cr alloy powder. Structures composed of Co-Cr alloys fabricated by the SLS method are used in manufacturing porcelain-fused-to-metal (PFM) restorations that are completed by firing ceramic powder.

Despite its aesthetic disadvantages, PFM has been routinely used in clinical cases because of its physical properties and biocompatibility.[6] The use of PFM also has other limitations, most notably with regard to the frauctured.[7] There are several factors that influence the fracture resistance of bonded metal-ceramics; however, among them, the coefficient of thermal expansion (CTE) difference is considered one of the most critical factors.[8,9] Reyes *et al.*[10] and Steiner *et al.*[11]

Corresponding author:
Ji-Hwan Kim
Department of Dental Laboratory Science and Engineering, Korea University, 145, Anam-ro, Seongbuk-gu, Seoul 02841, Republic of Korea
Tel. 82 2 940 2843: e-mail, kjh2804@korea.ac.kr
Received February 11, 2015 / Last Revision May 11, 2015 / Accepted May 13, 2015

The authors would like to thank E-Master Dental Hub Lab for processing this Co-Cr specimens with the EOS equipment.

 pISSN 2005-7806, eISSN 2005-7814

advised that in general, when metal and ceramic are used in the same restoration, the CTE of the metal should be slightly higher than that of the ceramic because of the compression stress generated during ceramic cooling. In addition, Craig and Ward suggested that the most desirable difference in the CTE for metal and ceramic is 0.5×10^{-6} m/m°C.[12] In order to prevent fracture induced by thermal expansion, manufacturing companies recommend using ceramic powder with an appropriate CTE difference when fabricating PFM restorations. However, clinicians are likely to select different ceramic powders based on other considerations such as the variety of powders available, economic feasibility,[13] aesthetics,[14] workability (work-related),[15] and mechanical properties.[16]

Long-term research and clinical use of conventional alloys has demonstrated that a variety of powders in addition to that recommended by the manufacturer can successfully be utilized for restorations. However, recommended powder (Vita VM13)[17] is used in restorations fabricated using a new additive manufacturing method because the introduction period of clinical cases has been brief, and hence there are not many related studies.

Thus, ceramic powders with different CTEs were selected to compare the bond strength between alloys fabricated by SLS and the ceramic powder. If differences in the bonding power are present, it will be confirmed clinically acceptable according to the ISO 9693 standard. If the difference is at a clinically acceptable level, then the range of powders available for clinicians and patients desiring restorations with appealing aesthetics and superior mechanical properties will be expanded. The null hypothesis is that the difference in the CTE does not affect the bonding power of ceramic-alloys fabricated by SLS.

MATERIALS AND METHODS

A total of 50 alloy specimens were fabricated and assessed as follows. To enable accurate comparison testing, Co-Cr alloy specimens (25.0 mm × 3.0 mm × 0.5 mm) were fabricated according to ISO 9693:1999[18] rather than in the anatomically correct tooth contour. The design was a flat surface that does not mimic common clinical designs. The specimens were designed flat most likely due to the fact that this is the only way a three point bend test can be done. And there is more accuracy than tooth contoured specimens.

The shape of the specimen was designed in three dimensions (3D) with Solidworks® software and converted to a STereoLithography (STL) file. STL files describe the surface geometry of a three-dimensional object CAD model attributes.[17]

The parameters of the SLS equipment (EOSINT M270; EOS Gmbh, Munich, Germany) used to make the alloy specimens from the converted file are as follows. SLS was performed using a Co-Cr alloy powder at a scan speed of 7 m/s, lamination thickness of 100 µm, Yb-fiber power of 200 W, fabrication speed of 20 m^3/s, laser spot size of 0.1 mm, and a particle size of 20 µm. These specifications are standards recommended by the manufacturer. The fabricated alloy specimens were abraded by airborne particles under 0.4 MPa of pressure. The particles used were 50 µm aluminum oxide particles (Cobra, Renfert GmbH, Hilzingen, Germany). Then, impurities on the surface were removed with ultrasonic cleaning and the surface was subjected to a steam cleaning. In order to inspect the surfaces of the alloy specimens, one was randomly selected and observed with a field emission scanning electron microscope (FE-SEM).

In this study, the Vita VM13 ceramic has the CTE that results in the most ideal CTE difference when compared to the Co-Cr alloy fabricated by SLS. Comparisons were made between the Vita VM13 and four ceramic powders (Duceram Kiss, Ceramco 3, Noritake EX-3, and Vintage MP) with different CTEs (Table 1) that are commonly used in the clinic for restorations using non-noble metals. By applying firing schedules appropriate for each powder as shown in Table 2, 8.0 mm long, 3.0 mm wide, and 1.0 mm high ceramic blocks were fabricated on the metal specimens.

In order to measure the metal-ceramic bond strength of each group, three point bending tests (ISO Standard 9693: 1999) were conducted using a universal testing machine (OTU-05D, Oriental TM Corp., Gyeonggi-do, Korea) with a crosshead speed of 1.5 mm/min.

Bond strength of the metal and ceramics was analyzed using descriptive statistics and one-way ANOVA testing (SPSS 12.0; SPSS Inc., Chicago, IL, USA) to evaluate whether any observed strength differences were a function of the differences in the CTE. The results of each group were tested at a significance level of α=.05.

Table 1. Coefficient of thermal expansion (CTE)of alloy and ceramic powders

Brand names	CTE (m/m°C) × 10^{-6}	Manufacturers	Lot No.
EOS SP2	14.0 - 14.5 (25 - 500°C)	EOS Gmbh, Munich, Germany	H051501
Vita VM13	13.1 - 13.6 (25 - 500°C)	VITA Zahnfabrik Bad Säckingen, Germany	17000
Duceram Kiss	13.0 (25 - 600°C)	DeguDent GmbH, Hanau, Germany	64982
Ceramco 3	12.6 (25 - 500°C)	Dentsply Ceramco, NJ, USA	11004612
Noritake EX-3	12.4 (25 - 500°C)	Noritake Kizai Co., Nagoya, Japan	053028
Vintage MP	12.3 (25 - 500°C)	Shofu Dental Corp, Kyoto, Japan	081263

Table 2. Firing schedules of veneering ceramics

Veneering ceramic (Group name)	Layer ceramic	Predrying of		Heating rate (°C/min)	Firing temp (°C)	Holding time (min)
		Temp (°C)	Time (min)			
Vita VM13 (VM)	opaque	500	4	75	920	1
	dentine	500	6	55	880	1
Duceram Kiss (Du)	opaque	575	7	55	930	2
	dentine	575	6	55	910	1
Ceramco 3 (Ce)	opaque	500	3	100	975	0
	dentine	650	5	55	930	0
Noritake EX-3 (No)	opaque	500	8	65	1000	1
	dentine	600	7	45	930	0
Vintage MP (Vi)	opaque	400	8	45	965	2
	dentine	400	6	45	920	0

* All specimens are under vacuum during heating.

RESULTS

The bond strength between the metal and ceramic was measured from samples of five groups of specimens, and no significant difference was observed in all groups (P>.05, Table 3). Analysis of the mean bond strength using descriptive statistics revealed that the Du group had the highest mean (61.18 ± 6.86 MPa), while the Vi group had the lowest (55.15 ± 7.53 MPa) (Table 4).

A minute gap is observed on the surface of the SLS specimen using FE-SEM. Upon magnification, it was determined that the gap exists between the additive manufactured layers of the surface and has a width of approximately 10 μm (Fig. 1).

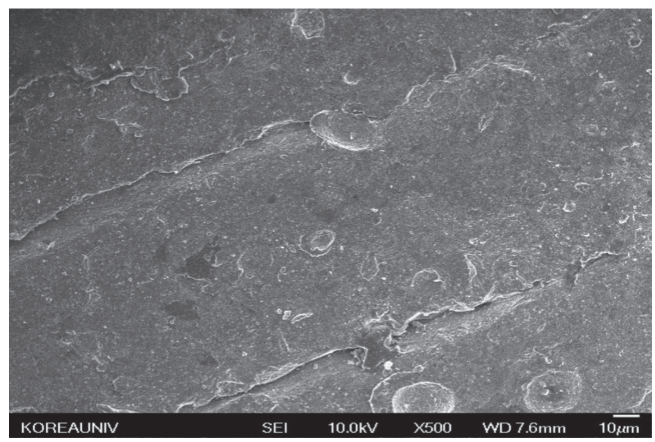

Fig. 1. Magnified view of the gap formation within Co-Cr alloy specimen.

Table 3. Results for one-way ANOVA

	Sum of squares	df	Mean square	F ratio	P value
Between groups	281.544	4	70.386	1.468	.228
Intergroup	2158.215	45	47.960		
Total	2439.759	49			

Table 4. Descriptive statistics for bond strength (MPa) of metal-ceramic

Group	N	Mean ± SD	Minimum	Maximum	Range (Max-Min)
VM	10	60.30 ± 7.14	46.93	71.48	24.55
Du	10	61.18 ± 6.86	51.13	71.91	20.78
Ce	10	58.87 ± 5.33	50.37	66.91	16.54
No	10	55.86 ± 7.53	44.27	67.13	22.86
Vi	10	55.15 ± 7.53	45.06	67.75	22.69

SD = standard deviation, Vita VM13 = VM, Duceram Kiss = Du, Ceramco 3 = Ce, Noritake EX-3 = No, Vintage MP = Vi.

DISCUSSION

The null hypothesis that the difference in the CTE does not affect the bonding power of ceramic-alloys fabricated by SLS was not rejected. Through the use of descriptive statistics, the mean bond strength values were, in descending order: Du (61.18 MPa), VM (60.30 MPa), Ce (58.87 MPa), No (55.86 MPa), and Vi (55.15 MPa). One-way ANOVA test results revealed no statistically significant differences and were not consistent with the manufacturer recommendation[17] that Vita VM13 ceramic powder would be the best fit for the SP2 Co-Cr alloy.

It is known that the CTE affects bond strength[19]; however, there are few studies describing the impact that the CTE range has on material properties. In this study, the differences were expected to be elucidated through use of materials with different CTEs, and in particular, a new dental technology called the additive manufacturing method, which is not a traditional method, was used.

The results of previous studies of the casting method using Co-Cr alloy were compared. An experiment by Korkmaz and Asar[20] resulted in mean bond strength of 58.44 MPa. In the study by Joias *et al.*,[21] the mean strength of five types of Co-Cr alloy was determined to be 61.40 MPa. In the bond strength study of Co-Cr alloy by Nieva *et al.*,[6] the range of values obtained was 57.11-63.81 MPa. In the study by Külünk *et al.*[22] using Co-Cr alloy, values of 41.73-54.55 MPa were demonstrated for the bond strength. When comparing the previous results with the values obtained in this study, the strengths were found to be similar.

When evaluating the difference in the CTE of the ceramics used in this experiment as compared to the metal (SP2), the range of values for Vita VM13, Duceram Kiss, Ceramco 3, Noritake EX-3, and Vintage MP are 0.4-1.4, 1.0-1.5, 1.4-1.9, 1.6-2.1, and 1.7-2.2 × 10^{-6} m/m°C, respectively. Although the results of research by Craig and Ward[12] indicated that a CTE difference of 0.5 × 10^{-6}°C would be the most optimal for the bond strength, some of the values from previous studies were found to be slightly higher.

The slight elevation observed can be attributable to the difference in SLS and casting restoration production methods. Fabrication in the casting method occurs after the complete dissolution of the metal while fabrication with SLS occurs by selectively sintering the metal powder. The thickness sintered at one time is about 100 µm and the particle size is about 20 µm. If a certain thickness is sintered, metal powder is scattered on it and sintering is carried out again. If this process is repeated, layers are formed with the desired additive thickness and a minute gap is generated on the metal surface between the layers. In addition, this process was inspected using FE-SEM and as a result, it was observed that gaps occurred between the surface layers of the metal specimens. The presence of gaps may widen the contact area of the metal and ceramic, resulting in the increase of the bond strength.[23] However, additional studies should be conducted to further analyze the cause of the increase.

The study by Wu *et al.*[3] used selective laser sintering of Co-Cr alloys and similarly to this study demonstrated that the bonding power is 57.78 ± 3.02 MPa. The authors indicated that the layer between the additive manufactured metal and ceramic is responsible for the good bonding strength observed. Also, in an experiment using a ceramic (CTE : 13.2 × 10^{-6} m/m°C) and Ni-Cr alloy (CTE : 14 × 10^{-6} m/m°C) fabricated by laser rapid forming of Liu *et al.*,[24] bond strength was found to be 44.7 MPa. Liu noted that the lamination that takes place during SLS might increase the bonding power between the metal and ceramic compared to the fabrication method based on a rapidly solidified point. In addition, he noted that pores or defects on the surface may improve the bond strength with the ceramic and are effective for use in PFM restorations, indicating that the result is similar to the gap formation observed in this study. The measured fracture values of all metals and ceramics of this experiment were determined to be higher than 25 MPa, the ISO 9693 standard. Similarity was observed when comparing SLS with conventional methods while meeting ISO standards.

In this study, the specimens with flat design were chosen because they were expected to have less experimental error compared to the specimens with actual crown contour. However, there is a definite need to re-examine the same procedure using the specimens with actual crown contour. The limitations of this study that the powders are made from different companies, which might lead to different properties other than CTE, need to be considered.

To obtain the same-sized specimens we used them by the following two steps: First, porcelain powder was veneered on a metal specimen (8.0 mm long, 3.0 mm wide, and 1.0 mm high) and any excessive parts were removed. Secondly, after firing the porcelain block was measured and re-veneered if any additional veneering was needed. The procedure was repeated until the size of a specimen was confirmed to have the exactly designed size.

Studies on a variety of restoration fabrication methods[25] have been conducted previously; however, there are few studies on SLS technology because it is a relatively new method. In order to apply a new technology to clinical practice safely and responsibly, important clinically relevant factors must be investigated. When compared with conventional methods, SLS has various advantages such as time shortening, work course shortening, and precise prostheses production. In order to successfully incorporate this technique into the clinic, additional studies should be performed.

CONCLUSION

The five powders evaluated in this study are all commonly used in clinical cases and have bond strength higher than the required minimum of 25 MPa. Moreover, no significant difference existed between the materials with regard to the evaluated mechanical properties. Therefore, it is concluded that a variety of powders can be applied to metal structures fabricated by SLS. In addition, the gap created in the surface layers of the alloy by the SLS method appears to positively affect the bonding power of metal-ceramic restorations.

ORCID

Eun-Jeong Bae *http://orcid.org/0000-0002-3098-7673*
Hae-Young Kim *http://orcid.org/0000-0003-2043-2575*
Woong-Chul Kim *http://orcid.org/0000-0002-6730-4960*
Ji-Hwan Kim *http://orcid.org/0000-0003-3889-2289*

REFERENCES

1. van Noort R. The future of dental devices is digital. Dent Mater 2012;28:3-12.
2. Moldovan O, Luthardt RG, Corcodel N, Rudolph H. Three-dimensional fit of CAD/CAM-made zirconia copings. Dent Mater 2011;27:1273-8.
3. Wu L, Zhu H, Gai X, Wang Y. Evaluation of the mechanical properties and porcelain bond strength of cobalt-chromium dental alloy fabricated by selective laser melting. J Prosthet Dent 2014;111:51-5.
4. Deckard CR. Method and apparatus for producing parts by selective sintering. United States Patent. US4863538 A. 1989 Sep 5.
5. Feygin M. Apparatus and method for forming an integral object from laminations. United States Patent US5354414 A. 1994 Oct 11.
6. Nieva N, Arreguez C, Carrizo R, Molé CS, Lagarrigue GM. Bonding strength evaluation on metal/ceramic interfaces in dental materials. Proc Mater Sci 2012;1:475-82.
7. Donovan TE. Porcelain-fused-to-metal (PFM) alternatives. J Esthet Restor Dent 2009;21:4-6.
8. Wataha JC. Alloys for prosthodontic restorations. J Prosthet Dent 2002;87:351-63.
9. Zinelis S, Tsetsekou A, Papadopoulos T. Thermal expansion and microstructural analysis of experimental metal-ceramic titanium alloys. J Prosthet Dent 2003;90:332-8.
10. Reyes MJ, Oshida Y, Andres CJ, Barco T, Hovijitra S, Brown D. Titanium-porcelain system. Part III: effects of surface modification on bond strengths. Biomed Mater Eng 2001;11:117-36.
11. Steiner PJ, Kelly JR, Giuseppetti AA. Compatibility of ceramic-ceramic systems for fixed prosthodontics. Int J Prosthodont 1997;10:375-80.
12. Craig RG, Ward ML. Restorative dental materials 10th ed. St. Louis, MO; Mosby; 1997.
13. Al Amri MD, Hammad IA. Shear bond strength of two forms of opaque porcelain to the metal substructure. King Saud Univ J Dent Sci 2012;3:41-8.
14. Barizon KT, Bergeron C, Vargas MA, Qian F, Cobb DS, Gratton DG, Geraldeli S. Ceramic materials for porcelain veneers: part II. Effect of material, shade, and thickness on translucency. J Prosthet Dent 2014;112:864-70.
15. Wang CH, Wu JH, Li HY, Wang PP, Lee HE, Du JK. Fracture resistance of different metal substructure designs for implant-supported porcelain-fused-to-metal (PFM) crowns. J Dent Sci 2013;8:314-20.
16. Souza JC, Henriques B, Ariza E, Martinelli AE, Nascimento RM, Silva FS, Rocha LA, Celis JP. Mechanical and chemical analyses across dental porcelain fused to CP titanium or Ti6Al4V. Mater Sci Eng C Mater Biol Appl 2014;37:76-83.
17. e-Manufacturing Solutions. Instructions for use: EOS Cobalt Chrome SP2. 2011 Available from: http://ip-saas-eos-cms.s3.amazonaws.com/public/32ff6c9b7964c1c9/7c73a9305d8007c47dec2e65196f09e5/EOS_CobaltChrome_SP2_en.pdf.
18. ISO 9693. Metal-ceramic dental restorative systems. 2nd ed. Geneva, Switzerland; International Organization for Standardization; 1999.
19. Lei YC. The influence of different thermal expansion coefficient (TEC) between ceramic and metal on thermal stability of porcelain-fused-to-metal (PFM) crown. Zhonghua Kou Qiang Yi Xue Za Zhi 1991;26:329-32, 388.
20. Korkmaz T, Asar V. Comparative evaluation of bond strength of various metal-ceramic restorations. Mater Des 2009;30:445-51.
21. Joias RM, Tango RN, Junho de Araujo JE, Junho de Araujo MA, Ferreira Anzaloni Saavedra Gde S, Paes-Junior TJ, Kimpara ET. Shear bond strength of a ceramic to Co-Cr alloys. J Prosthet Dent 2008;99:54-9.
22. Külünk T, Kurt M, Ural Ç, Külünk Ş, Baba S. Effect of different air-abrasion particles on metal-ceramic bond strength. J Dent Sci 2011;6:140-6.
23. Bae EJ, Kim JH, Kim WC, Kim HY. Bond and fracture strength of metal-ceramic restorations formed by selective laser sintering. J Adv Prosthodont 2014;6:266-71.
24. Liu Y, Wang Z, Gao B, Zhao X, Lin X, Wu J. Evaluation of mechanical properties and porcelain bonded strength of nickel-chromium dental alloy fabricated by laser rapid forming. Lasers Med Sci 2010;25:799-804.
25. de Melo RM, Travassos AC, Neisser MP. Shear bond strengths of a ceramic system to alternative metal alloys. J Prosthet Dent 2005;93:64-9.