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RESEARCH AND EDUCATION

Effects of heat treatment on metal-ceramic combination of selective-laser-melted cobalt-chromium alloy

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ABSTRACT

Statement of problem. Components fabricated by selective laser melting (SLM) deform because of residual stress, but heat treatment allows the release of that stress and avoids deformation. Although dental cobalt-chromium (Co-Cr) alloy has been specifically designed for SLM, the effects of heat treatment on the metal-ceramic combination of SLM Co-Cr restorations require investigation.

Purpose. The purpose of this in vitro study was to evaluate the effects of heat treatment on the metal-ceramic combination of SLM Co-Cr alloy.

Material and methods. Following ISO 9693:2012, Co-Cr metal strips (Solibond C Plus cast alloy and SLM powders; YETI Dental) were fabricated with a dimension of 25×3×0.5 mm by casting and SLM. The SLM specimens were divided into 3 subgroups (n=15 for each subgroup). Two subgroups were subjected to heat treatment at 880°C (SLM-880) and 1100°C (SLM-1100). The third subgroup was not subjected to heat treatment and served as a control (As-SLM). Cast specimens (n=15) also acted as a control. A porcelain layer with a thickness of 1.1 mm was fired to the central area (3×8 mm) of each specimen. The 3-point bend test was used to evaluate the metal-ceramic bond strength (τ_b). The fractured metal surfaces were examined by the naked eye, using a digital camera, and also using a scanning electron microscope. The area fraction of adherence porcelain (AFAP) was determined by measuring the atomic percentage of silicon using energy-dispersive x-ray spectroscopy (EDS). One-way ANOVA and the Kruskal-Wallis test, followed by the Mann-Whitney test (α=.05), were used for statistical analysis.

Results. The 1-way ANOVA found no significant difference in the bond strength among the 4 groups. The EDS analysis indicated that specimens in the groups receiving heat treatment (SLM-880 and SLM-1100) showed higher AFAP values than those in the As-SLM group ($P<.05$). The SLM-880 also showed significantly higher AFAP values than the SLM-1100. Compared with the cast group, significant differences in AFAP values were also observed, and the specimens in the order of highest to lowest AFAP values were SLM-880>cast>As-SLM; no significant difference was found between the SLM-1100 and cast groups.

Conclusions. Heat treatment at 880°C and 1100°C did not affect the metal-ceramic bond strength of Co-Cr alloy made by SLM but did improve the porcelain adherence. SLM-fabricated and heat-treated Co-Cr alloy shows comparable or more porcelain adherence than cast specimens. (J Prosthet Dent 2018;120:319.e1-e6)

Selective laser melting (SLM) is a recently introduced manufacturing technique for the metal substructure of metal-ceramic restorations, offering rapid production and materials with excellent properties.[1,2] During the SLM process, a computer-aided design (CAD) system directs a laser beam to fuse metal powders to produce a precise layer of the component. Subsequent layers are overlapped on the solidified layer, and the laser beam is directed according to the next data specifications; this continues until all slices of data have been executed and the components have been formed.[2,3]

One concern is that the high-temperature gradient in the SLM process may cause the cooling rate and the cooling shrinkage force of the melted metal powder to vary with the position of the laser-scanning path.[4-6] Any uneven shrinkage of the solidified

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Clinical Implications

Heat treatment to release stress and avoid distortion is necessary for dental restorations made by selective laser melting. Heat treatment does not affect the metal-ceramic bond strength but does improve the porcelain adherence of selective-laser-melted Co-Cr alloy.

material can lead to residual stress.[4-7] With the accumulation of residual stress between and within layers, the stress increases, gradually resulting in warpage, deformation, and cracking of the fabricated components.[4-7] Although distortion can be limited by the use of a metal support structure, residual stresses inside the support and components should be reduced as much as possible before components, especially long-span prostheses, are removed from the metal base.

The microstructures and mechanical properties of alloys depend on heat treatments.[8-10] Heat treatment is also applied to eliminate the crystal defects of alloys, such as dislocations, which stabilizes the microstructure and reduces residual stress.[10] Heat treatment has been considered necessary to release residual stress after manufacturing prostheses with SLM.[6,7,11,12]

In a metal-ceramic system, adequate bond strength is essential.[13] Scanning electron microscopy (SEM) and energy-dispersive x-ray spectroscopy (EDS) can be used to evaluate porcelain adherence and examine fracture modes.[14-18] The strength of porcelain fused to SLM-fabricated Co-Cr alloy was reported as comparable with that of traditional casting and sufficient to comply with ISO 9693 requirement for τ_b>25 MPa.[13,16,17] Xiang et al[16] and Li et al[17] reported that the SLM metal-ceramic system exhibited better porcelain adherence than materials prepared by conventional casting, and Ren et al[18] reached the same conclusion for specimens subjected to multiple firings. A recent study has shown that the choice of SLM Co-Cr alloy powders affects porcelain bond strength but that the layer thickness of the powder in the SLM process does not affect bond strength.[19] However, the authors did not discuss the potential effects of heat treatment to release stress on the metal-ceramic combination of Co-Cr alloy fabricated by SLM.

The purpose of this in vitro study was to investigate the metal-ceramic bond strength and porcelain adherence of SLM Co-Cr alloy exposed to 2 different heat treatments and using SLM specimens without heat treatment and cast Co-Cr alloys as controls. The null hypotheses were that the bond strength and area fraction of adherence porcelain (AFAP) would not vary with heat treatment.

MATERIAL AND METHODS

Cast Co-Cr metal block and SLM powder with the same compositions (Solibond C PLUS; Co, 63%; Cr, 24%; W, 8.1%; Mo, 2.9%; Nb, 0.9%; Si, 1.1%; particle size, 10 to 63 μm; YETI) were used. Four groups, designated cast, As-SLM, SLM-880, and SLM-1100, were prepared, and 15 metal strips (25×3×0.5 mm)[13] were fabricated for each group. The cast specimens were fabricated in a vacuum casting furnace (Argoncaster; Shofu Inc), and all selective-laser-melted specimens were fabricated in an SLM machine (M100; EOS). As illustrated in Figure 1, after the SLM specimens were prepared, the SLM-880 group specimens were subjected to a heat treatment at 880°C, and the SLM-1100 group specimens were heat-treated at 1100°C. These heat treatment processes were derived from the instructions for use of EOS Co-Cr SP2 and EOS Co-Cr RPD alloys.[20]

The metal strips were then wet-ground with 400-grit Al_2O_3 paper, ultrasonically rinsed in deionized water for 5 minutes, air-dried, subjected to preoxidation (for 5 minutes at 950°C according to the manufacturer of the alloy), and airborne-particle abraded with 110-μm Al_2O_3. A layer of opaque porcelain and a layer of body porcelain (IPS Classic; Ivoclar Vivadent AG) were then applied to the central area (3×8 mm) of each metal strip to form a 1.1-mm-thick porcelain veneer in accordance with ISO 9693:2012.[13] All specimens were fired 4 times during the veneering process in a porcelain furnace (Multimat NTX^{press}; Dentsply Sirona).

The 3-point bend test[13] was performed in a universal mechanical testing machine (3367; Instron) at a constant rate of 1.5 mm/min. The specimens were positioned on 2 cylindrical metal supports with a radius of 1 mm and a span of 20 mm. The ceramic was positioned on the side opposite to the applied force. The load was applied at the midpoint of each metal strip until a sudden drop in the load-deflection curve occurred, indicating bond failure. The failure load was recorded, and the debonding strength for each specimen was calculated according to $\tau_b = \kappa \cdot F_{fail}$, $\kappa = f\ (d_m, E_m)$[13], where F_{fail} is the load at debonding (N), d_m is the thickness of the metal substrate, E_m is the modulus of elasticity of metal (210 GPa, as provided by the manufacturer), and κ is calculated from d_m and E_m.

The fracture surfaces of the specimens were examined by the naked eye, using a digital camera (DS126201; Canon Inc), and SEM (EVO 18; Carl Zeiss Jena). EDS equipped in the SEM system was used for a raster scan of the central region of the specimens at ×40 magnification. The percentage AFAP was evaluated according to the equation AFAP=$(Si_f\text{-}Si_m)/(Si_o\text{-}Sim)$,[14-18] where Si_m is the atomic percentage of silicon on the specimen surface (Si, Al, Co, Cr, and W) before application of the opaque porcelain, Si_o is the atomic percentage of silicon on the

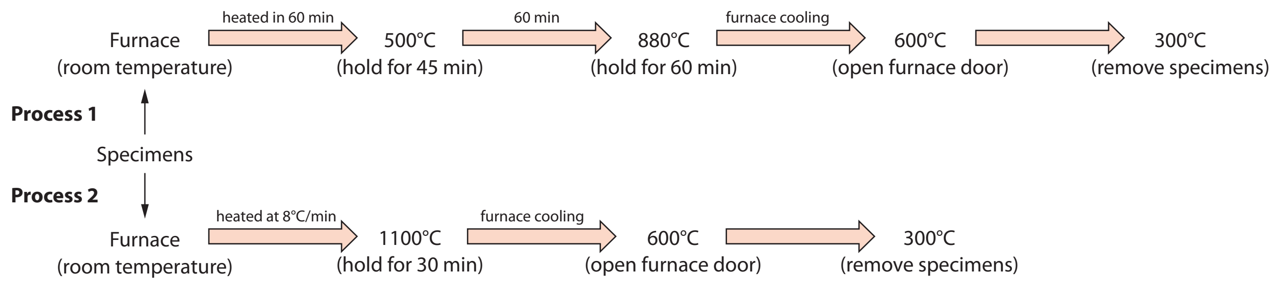

Figure 1. Heat treatments tested.

specimen surface (Si, Al, Na, K, Ca, Zr, and Zn) after the fusion of the opaque porcelain, and Si_f is the atomic percentage of silicon on the specimen surface (Si, Al, Co, Cr, W, Na, K, Ca, Zr, and Zn) after the debonding of the porcelain veneer.

All analyses were conducted using a statistical software program (IBM SPSS Statistics v24.0; IBM Corp). One-way ANOVA and the Kruskal-Wallis test, followed by the Mann-Whitney test (α=.05), were used for statistical analysis.

RESULTS

The τ_b and AFAP values and the standard deviations for each group were determined and are shown in Table 1. For the τ_b analysis, the variability among the 4 groups was homogeneous (*df1*=3; *df2*=56; *P*=.083), and 1-way ANOVA demonstrated no significant differences in bond strength (*df*=3; *F*=1.172; *P*=.329).

For the AFAP analysis, the variability was heterogeneous (*df1*=3; *df2*=56; *P*=.023). The Kruskal-Wallis test showed significant differences in the AFAP values among the 4 groups (*P*<.001), and the Mann-Whitney test showed significant differences among the groups (*P*<.05) except between the cast and SLM-1100 groups (*P*=.325). Compared with the cast group, the specimens in the order of highest to lowest AFAP values were SLM-880>cast>As-SLM.

From the digital image (Fig. 2), all fractured surfaces appeared to have a thin layer of ceramic remnant on the metal substrate. Representative SEM images (Fig. 3) for each group were almost identical. The spot EDS analysis indicated a location with a ceramic remnant (Fig. 4A) and another with a mixture of the ceramic and metal (Fig. 4B).

DISCUSSION

This study was designed to evaluate the effects of heat treatment on the metal-ceramic bond strength and porcelain adherence of a Co-Cr alloy fabricated by SLM. No significant differences in the bond strength were observed for the As-SLM, SLM-880, and SLM-1100 groups, leading to the acceptance of the first null hypothesis. However, as the SLM-880 and SLM-1100 groups showed significantly higher AFAP values than the As-SLM group, the second null hypothesis was rejected.

Table 1. τ_b (MPa) and AFAP (%) values (±SD) of groups tested

Group	n	τ_b	AFAP
Cast	15	41.7 ±4.02	68.0 ±5.34
As-SLM	15	43.4 ±7.20	62.3 ±6.18
SLM-880	15	42.8 ±6.07	75.1 ±2.92
SLM-1100	15	45.7 ±6.44	71.1 ±4.49

τ_b, metal-ceramic bond strength; AFAP, area fraction of adherent porcelain; SLM, selective laser melting. As-SLM, not subjected to heat treatment. SD, standard deviation. SLM-880, heat treatments at 880°C. SLM-1100, heat treatment at 1100°C.

Heat treatment can reduce and eliminate residual stresses in a metal.[10] The equilibrium phase diagram of Co-Cr alloys indicates that at >900°C, the expected structure is face-centered cubic and that at <900°C, it is hexagonal close-packed.[9] In general, the face-centered cubic structure exhibits ductility, and the hexagonal close-packed structure leads to more brittleness.[9] Because of this, 2 stress-relief processes, below or above 900°C, were used. For example, the stress-relief processes of EOS Co-Cr alloy SP2 and EOS Co-Cr RPD[20] have been described for SLM-fabricated dental prostheses. In addition, treatment of Co-Cr alloys at a temperature of 1100°C allows recovery, recrystallization, and grain regrowth, which together can change the grain morphology of the alloy.[21]

In combinations of alloys and porcelain, chemical bonding is essential and is affected by the composition and thickness of oxide film on the metal surface.[22,23] The metal oxide film forms atomic bonds with the metal oxides in the ceramic,[22-24] but an excessively thick oxide film could decrease the metal-ceramic bond strength.[24] In this study, airborne-particle abrasion was performed after preoxidation. This process removes surface debris and excessive oxide film, improves the wettability of the porcelain, and strengthens mechanical retention.[24] In debonding studies of dental metal-ceramic restorations, adhesive fracture is defined as the failure of the metal-ceramic interface area, and cohesive fracture is defined as failure that occurs entirely within the porcelain.[16,17,23] Cohesive fracture indicates the optimal metal-ceramic

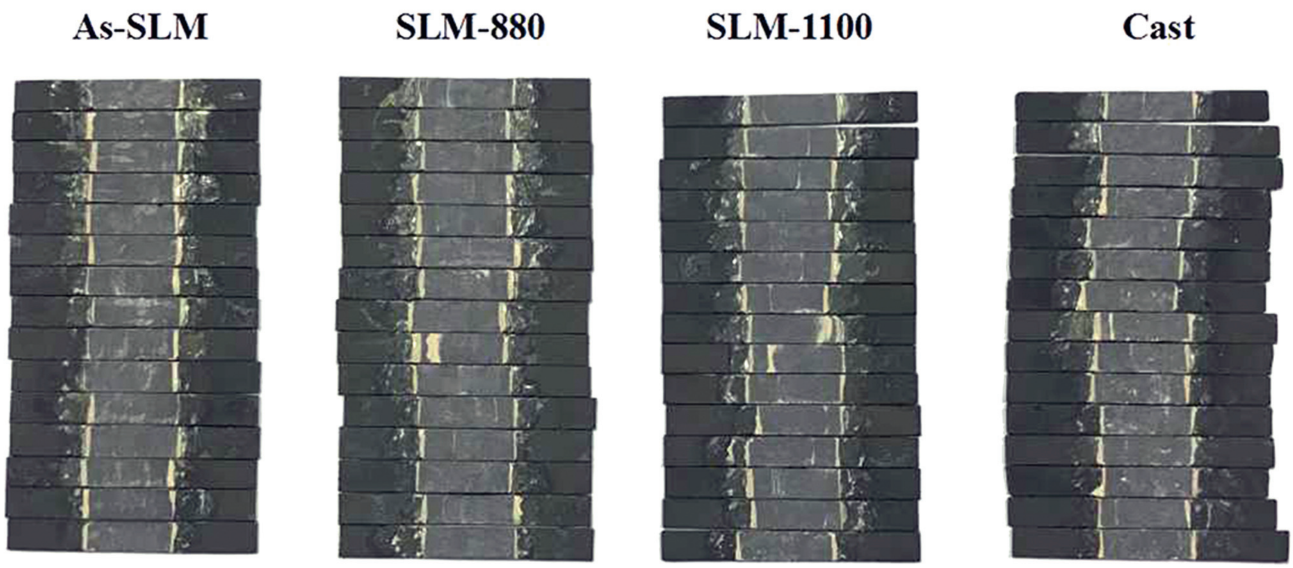

Figure 2. Digital image of specimen surfaces after fracture failures. As-SLM, not subjected to heat treatment. SLM-880, heat treatments at 880°C. SLM-1100, heat treatment at 1100°C.

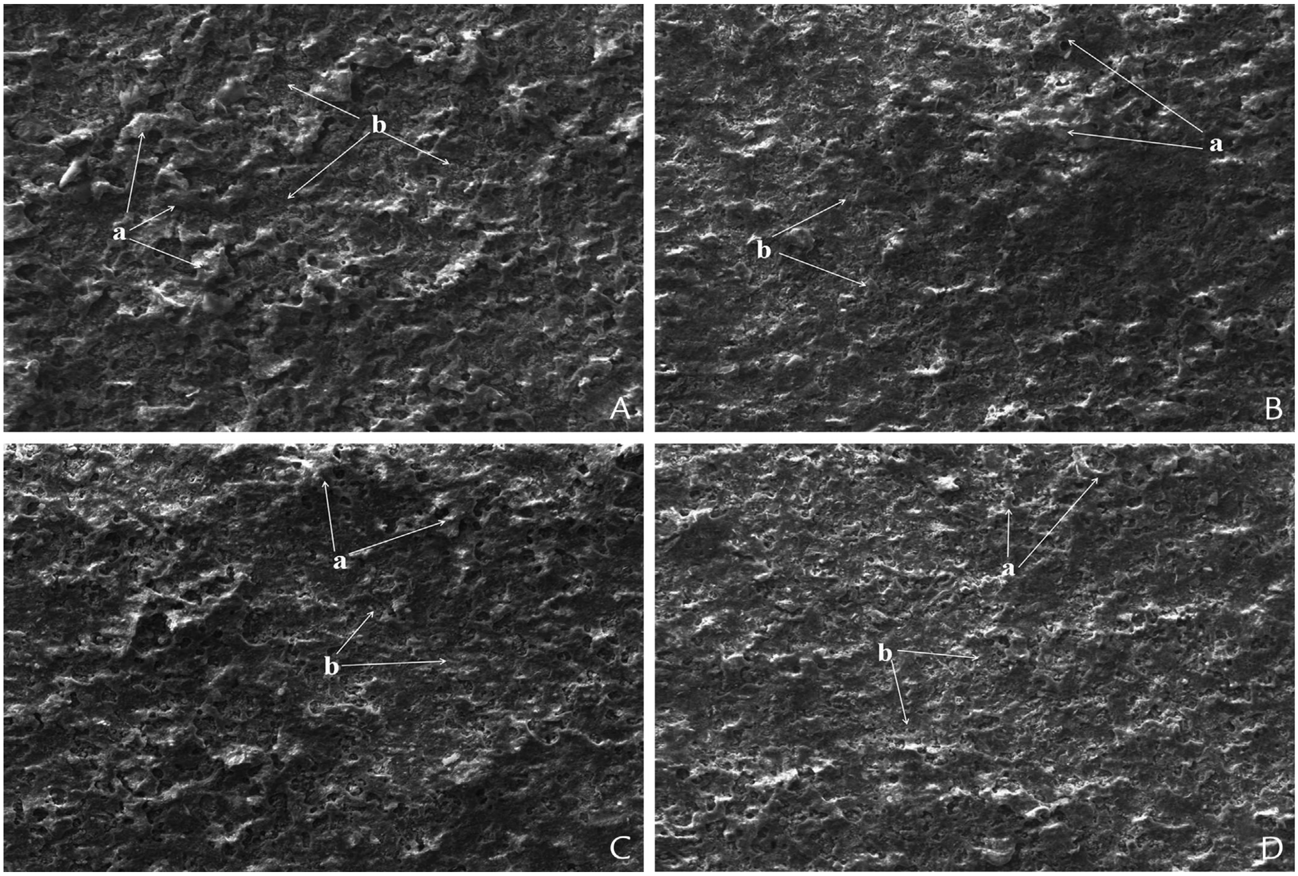

Figure 3. Scanning electron micrographs of fractured metal surfaces. A, As-SLM. B, SLM-880. C, SLM-1100. D, cast. (20.0 kV, original magnification ×250). *Arrows* labeled "a" and "b" indicate representative spot EDS scanning spectrum in Figure 4. As-SLM, not subjected to heat treatment. EDS, energy-dispersive x-ray spectroscopy. SLM-880, heat treatments at 880°C. SLM-1100, heat treatment at 1100°C.

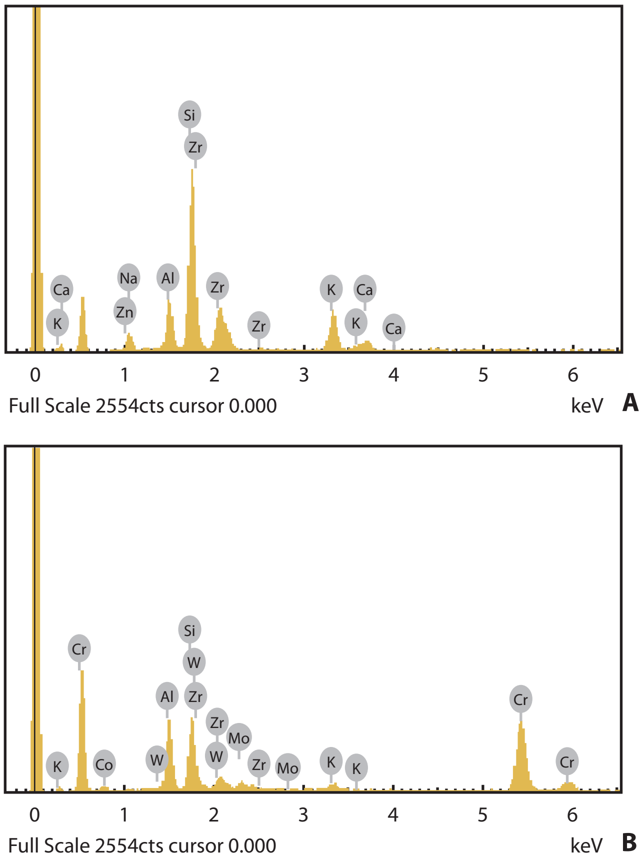

Figure 4. Representative spot EDS scanning spectrum of the arrows "a" and "b" in Figure 3. A, "a". B,"b". EDS, energy-dispersive x-ray spectroscopy.

combination, implying that the bond of the metal-ceramic interface area is stronger than that within the porcelain.[16,23] However, no direct relationship has been reported between failure type and metal-ceramic bond strength.[16,19] A recent study proposed that the application of failure classification is not necessary.[19] In the present study, all fractured metal surfaces exhibited surface differences, with some areas, such as those indicated with "a" in Figure 3, containing only the remnant ceramic and with other regions, such as those indicated with "b" in Figure 3, showing a mixture of remnant ceramic and metal, indicating a mixture of adhesive and cohesive failure as reported in previous studies.[16,17]

A correlation between silicon radiograph counts and AFAP has been demonstrated,[14] and AFAP analysis was applied as an additional means of evaluating the porcelain adherence of the metal copings.[14-18] Studies[18,25] have shown that repeated firings of porcelain weaken the compatibility between the cast alloys and the ceramic and decrease the bond strength, but this was not observed in SLM Co-Cr specimens; after 5 or 7 firings, the SLM Co-Cr alloy exhibited more mean AFAP than after 3 firings.[18] Repeated firings serve as a heat treatment and could change the microstructure of the alloy.[26] A recent study[27] has shown that adhesion between Co-Cr alloy and porcelain is inversely proportional to the hardness of the interfacial layer at the metal surface. At the lower hardness interfacial zone, the additional plastic energy was consumed during the extension of the crack along the more ductile interface area of the metal, resulting in higher adhesion energy at the interfacial zone.

In the present study, SLM Co-Cr alloy that was heat-treated at 880°C or 1100°C showed significantly higher AFAP values, indicating more porcelain adherence than the specimens prepared without heat treatment. This may reflect different metallurgic structures and changes in the hardness of the alloy before and after heat treatment. Besides, SLM-880 showed higher AFAP values than SLM-1100 ($P<.05$), demonstrating that different heat treatments had different effects on the porcelain adherence of SLM Co-Cr alloy. The metallurgic structures of As-SLM and cast Co-Cr alloys were distinct although they had similar compositions.[3,17,26] The structure of traditional cast Co-Cr alloy is composed of large dendrites, and As-SLM Co-Cr alloy has fine cellular dendrites caused by the rapid cooling and high-temperature gradients.[3,17,26] The As-SLM group had significantly lower AFAP values than the cast specimens, a finding that was inconsistent with previous studies. The rough base metal surface promotes mechanical interlocking between the porcelain and metal,[28,29] which should result in greater porcelain adherence. In this study, each specimen was wet-ground with 400-grit Al_2O_3 paper and abraded with 110-μm Al_2O_3 particles, but previous studies[16-18] did not specify whether a grinding step was performed, how specimens were ground, or whether the specimens were ground in a consistent manner, which could explain the different results. Regardless, the SLM-fabricated and heat-treated Co-Cr alloy showed comparable porcelain adherence (SLM-1100) or more porcelain adherence (SLM-880) than the cast specimens.

Although AFAP values were significantly different among the groups, significant differences were not found for the metal-ceramic bond strength. A previous study also reported no correlation between the bond strength and AFAP.[30] However, the 3-point bend test may be a flawed way of evaluating bond strength and may not be representative of the clinical situation.[16,18] Therefore, whether the AFAP measurement (porcelain adherence or ceramic remnants on the fractured metal surface) has decisive significance for the metal-ceramic combination or adequately represents the clinical situation requires further study. As in the present study, significant differences in the porcelain adherence between groups have been reported, without significant differences in bond strength.[16-18] New quantitative methods of evaluating the combination of the metal and porcelain are worth exploring.

The current results indicate that heat treatment improved porcelain adherence. However, the mechanism and metallurgical structures of SLM Co-Cr alloy before and after heat treatment require further investigation. The residual stress produced in the SLM process is known in the dental additive manufacturing industry but may be poorly understood by dental laboratories and dentists. Overall, additional studies are required to examine more fully the effect of stresses on clinical application performance of SLM dental prostheses, including metal base fitness and mechanical property.

CONCLUSIONS

Based on the findings of this in vitro study, the following conclusions were drawn:

1. Heat treatment at 880°C or 1100°C did not affect the metal-ceramic bond strength of SLM-fabricated Co-Cr alloy but did improve porcelain adherence.
2. SLM-fabricated and heat-treated Co-Cr alloy shows comparable (SLM-1100) or better porcelain adherence (SLM-880) than that of cast specimens.

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