

# Evaluation of Bonding Behavior of Silver-Tin-Zinc-Indium Alloy to Adhesive Luting Cements

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**Abstract** - The bond strengths of a silver-tin-zinc-indium alloy used with adhesive luting cements were investigated. The metal surfaces were primed with two metal conditioners designed for noble metal alloys or base metal alloys, or prepared using a Rocatec tribochemical coating unit. Two adhesive luting cements (Super-Bond C&B and Panavia F 2.0) were applied. It can be concluded that airborne-particle abrasion with alumina was effective, but the effects on the bond durability of both the metal conditioners and the tribochemical silica coating method were not clear. Such bonding behavior seems to be particular to this kind of silver-rich dental casting alloy.

KEY WORDS: adhesive luting cements, bonding, metal conditioner, silver-tin-indium alloy, tribochemical coating

## INTRODUCTION

Silver-based casting alloys serve as substitutes for gold alloys in the dental clinic and are mainly indicated for use in dowel-and-core restorations<sup>1</sup>. The long-term clinical success of a dowel-and-core restoration is desirable, and this success greatly depends on the retention of the dowel on the tooth structure. It was reported that the mould filling capability of silver-zinc-tin-indium alloy is superior to that of silver-palladium-copper-gold alloy using a conventional centrifugal casting machine<sup>2</sup>. However, cast dowel-and-core restorations sometimes fail due to separation, chiefly at the dowel-tooth interface. Therefore, strengthening the interface is important, and the use of adhesive resin luting cements is reported to enhance dowel retention<sup>3,4</sup>.

Little information, however, is available with regard to the bonding behavior of silver-rich alloys treated with adhesive luting cements<sup>5,6</sup>. The purpose of the present study was to investigate the bond strengths of a silver-tin-zinc-indium alloy primed with adhesive luting cements using current metal conditioning methods.

## MATERIALS AND METHODS

A total of 250 disc-shaped wax patterns (approximately 10.0 mm in diameter and 2.5 mm thick) were cast with a silver-tin-zinc-indium alloy (Miro Bright) in a cristobalite investment material (Cristobalite Micro II) using a conventional spring-driven centrifugal casting machine (Kerr Centrifico casting machine). The disc surfaces were finished with 600-grit silicon-carbide abrasive paper under running water (Group 1). The polished surfaces were then airborne particle-abraded with 50 µm grain-sized alumina (Aluminous Powder WA 360) for 10 seconds at an emission pressure of 0.48 MPa using a grit blaster (Micro Blaster)

(Group 2). One of the two metal conditioners tested, Metaltite (Group 3) or Estenia C&B Opaque Primer (Group 4) was applied to the airborne particle-abraded surfaces using a sponge pellet. Metaltite contains 6-methacryloxyhexyl 2-thiouracil-5-carboxylate (MTU-6), and Estenia C&B Opaque Primer contains 10-methacryloyl-oxydecyl dihydrogen phosphate (MDP), according to the respective manufacturers' product information. MTU-6 is one of the functional monomers designed for noble metal alloys, and MDP is designed for base metal alloys. In Group 5, the surfaces finished with 600-grit silicon-carbide abrasive paper were prepared in a Rocatec<sup>®</sup> junior coating unit according to the manufacturer's instructions. Sticky masking tape with a 6.0 mm diameter circular hole was placed on the center of the bonding surface of each disc, and a Teflon ring (5.0 mm inner diameter, 6.0 mm outer diameter) was put into the hole of the masking tape to hold it in place. Thus, the bonding area was defined by the inner diameter of the Teflon ring. The two adhesive luting cements, Super-Bond C&B Ivory and Panavia F 2.0, were mixed according to the manufacturers' instructions, and one of them was applied inside the Teflon ring on each specimen. After the adhesive luting cement was set, the masking tape and Teflon ring were removed as gently as possible, and the specimen was completed. All the specimens were immersed in water at 37°C for 24 hours; five sets of ten specimens were tested for 24-hour shear bond strength. The other five sets of ten specimens were placed in a thermocycling apparatus (Thermal Shock Tester TTS 1) and thermocycled in water for 10,000 cycles between 5°C and 55°C with a dwell time of 1 minute at each temperature. For the specimens treated with Super-Bond C&B, an additional 20,000 thermocycles were also performed. A compressive load was applied to each specimen in a shear testing apparatus, and the shear bond strengths were determined using a universal testing machine (Autograph AGS-J) at a crosshead speed of 1.0 mm/min.

The means and standard deviations for the shear bond strengths (n=10) were calculated and analyzed using statistical computer software (STATISTICA for Windows Version 5.5). An analysis of variance (ANOVA) and the

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Student-Newman-Keuls post-hoc comparisons test was performed at the 0.05 level of significance.

The type of bond failure was determined after shear testing by examining the fracture surfaces using an optical microscope (Nikon 92052) at 30X magnification. Failure was classified as A (adhesive failure at the metal-resin interface), C (cohesive failure within the resin) or M (mixture of adhesive failure and cohesive failure).

## RESULTS

The average shear bond strengths of the specimens and the standard deviations (SD) for Super-Bond C&B and Panavia F 2.0 are summarized in Tables 1 and 2 with statistical significance. The statistical analysis divided the results of Super-Bond C&B into five statistically significant groupings (a-e) in Table 1. The shear bond strengths of groups 2 and 3 were greater than those of the other groups before thermocycling. There were no significant differences ( $p>0.05$ ) in the bond strength among groups 2-5 after 10,000 thermocycles, and among groups 2, 3 and 5 after 20,000 thermocycles. The shear bond strength of group 1 was extremely low after 10,000 thermocycles, and adhesive failure occurred in all specimens (Table 3).

The bond strengths of Panavia F 2.0 were inferior to those of Super-Bond C&B. The statistical analysis divided the results of Panavia F 2.0 into three statistically significant groupings (a-c) in Table 2. They indicated that 10,000 thermocycles did not significantly ( $p>0.05$ ) decrease the bond strength in all groups except for group 1. There were no significant differences ( $p>0.05$ ) in the bond strength among all groups except for group 1 both before and after thermocycling.

The modes of failure of all specimens are presented in Tables 3 and 4. There were no cohesive failures in the present study. The largest number of mixed failures was found in groups 2, 3 and 5 in both cements after thermocycling.

## DISCUSSION

The present study compared the shear bond strength and durability of a silver-tin-zinc-indium alloy to two adhesive luting cements in combination with surface preparations. Matsumura *et al.*<sup>5,6</sup> reported that the combined use of thiol-based metal conditioners and Super-Bond C&B effectively bonded to noble metal alloys, with the exception of the silver-indium alloy. It was reported that gold alloys (Type IV and 14K), a silver-palladium alloy and a silver-copper alloy modified by a liquid gallium-tin alloy<sup>7,8</sup> showed high bond strength to Super-Bond C&B as well as water durability, but this liquid alloy did not promote the bonding to a silver-indium alloy or to base-metal alloys. These studies strongly indicated that the bonding behavior of silver-rich alloys may differ from that of the other noble metal alloys.

The silver-rich alloys tested in past studies were a silver-indium alloy<sup>5-8</sup> or a silver-tin alloy<sup>7</sup>. It appears that the present study is the first to investigate the bonding of a silver-tin-zinc-indium alloy treated with Panavia F 2.0 or

Rocatec tribochemical coating<sup>10</sup>. As shown in the present results, adhesive luting cement considerably affected the bond strengths of the silver-tin-zinc-indium alloy, i.e., Super-Bond C&B was superior to Panavia F 2.0. This finding clearly indicated the character of the luting cements even before thermocycling. One noticeable characteristic of the Super-Bond C&B groups was that they showed almost the highest bond strength values, including the specimens without preparation. However, thermocycling considerably decreased the bond strength of the surfaces finished with 600-grit silicon-carbide abrasive paper. Matsumura *et al.*<sup>5,6</sup> reported that the bond durability of silver-indium alloy was poor after thermocycling and speculated that the reason was that the corrosion resistance of this alloy was insufficient at the interface. It is known that the silver-rich alloys corrode very quickly<sup>8</sup>. In the present study, however, there were no significant differences among the airborne-particle abrasion group, the MTU-6 conditioner group, and the tribochemical silica coating group after 20,000 thermocycles. In the MDP conditioner group, the targets were the base metal components of the alloy tested, such as zinc, tin and indium, but the bond strength after 20,000 thermocycles was not superior to those of the other groups except for the group without preparation. The chemical composition of this alloy is 72 mass% silver, 13 mass% zinc, 9 mass% tin and 6 mass % indium, which was obtained from the manufacturer's product information. The reason why there was no effect of MDP conditioner may be the low content of these base metal components. Further investigation by testing at more than 20,000 thermocycles is needed to determine the most effective preparation method for a silver-tin-zinc-indium alloy with Super-Bond C&B.

The tribochemical silica coating method includes two airborne-particle abrasion steps to prepare the metal surface prior to the application of the silane and resin. It was reported that the silica-coated alloys improved the chemo-mechanical bonding in a high noble gold-silver-copper, a nickel-chromium and a cobalt-chromium alloy. Embedded alumina particles were found in these alloys after airborne particle abrasion<sup>10</sup>. According to the manufacturer's product information, the Vickers hardness of the silver-tin-zinc-indium alloy is 145, which is a comparatively low value. It is speculated that the low hardness contributes to the insufficient tribochemical silication because of the weak bonding between the silica layer and metal surface.

## CONCLUSION

In conclusion, the bond strength of Super-Bond C&B was superior to that of Panavia F 2.0 to a silver-tin-zinc-indium alloy. Airborne particle abrasion with 50  $\mu\text{m}$  grain-sized alumina was effective at improving the bond durability of the adhesive luting cements. In the present study, however, the effects on the bond durability of both the metal conditioner designed for noble metal alloys and the tribochemical silica coating method were not clear even after 20,000 thermocycles.

**Table 1.** Bond strengths (MPa) to Super-Bond C&B before and after thermocycling

| Group* | Thermocycles |     |              |                |     |              |               |     |              |
|--------|--------------|-----|--------------|----------------|-----|--------------|---------------|-----|--------------|
|        | 0 cycles     |     |              | 10, 000 cycles |     |              | 20,000 cycles |     |              |
|        | Mean         | SD  | Significance | Mean           | SD  | Significance | Mean          | SD  | Significance |
| 1      | 21.4         | 2.7 | b            | 0.8            | 0.7 | f            | 0.0           | 0.0 | f            |
| 2      | 23.3         | 1.1 | a            | 19.9           | 0.9 | b, c         | 20.0          | 1.3 | b, c         |
| 3      | 23.8         | 0.7 | a            | 19.6           | 2.2 | b, c         | 17.7          | 1.0 | b, c, d      |
| 4      | 19.7         | 1.1 | b, c         | 19.0           | 0.9 | b, c         | 16.0          | 1.8 | c, d, e      |
| 5      | 19.4         | 2.1 | b, c         | 17.9           | 1.4 | b, c         | 18.3          | 1.3 | b, c         |

**Table 2.** Bond strengths (MPa) to Panavia F 2.0

| Group* | Thermocycles |     |              |                |     |              |
|--------|--------------|-----|--------------|----------------|-----|--------------|
|        | 0 cycles     |     |              | 10, 000 cycles |     |              |
|        | Mean         | SD  | Significance | Mean           | SD  | Significance |
| 1      | 5.8          | 1.9 | b            | 0.8            | 2.0 | c            |
| 2      | 11.4         | 1.2 | a            | 12.3           | 4.1 | a            |
| 3      | 11.8         | 2.9 | a            | 11.0           | 3.2 | a            |
| 4      | 11.9         | 2.2 | a            | 13.0           | 4.3 | a            |
| 5      | 12.6         | 2.5 | a            | 13.4           | 2.6 | a            |

**Table 3.** Failure mode of Super-Bond C&B

| Group* | Thermocycles |   |   |                |   |   |               |   |   |
|--------|--------------|---|---|----------------|---|---|---------------|---|---|
|        | 0 cycles     |   |   | 10, 000 cycles |   |   | 20,000 cycles |   |   |
|        | A            | M | C | A              | M | C | A             | M | C |
| 1      | 5            | 5 | 0 | 10             | 0 | 0 | 10            | 0 | 0 |
| 2      | 5            | 5 | 0 | 7              | 3 | 0 | 7             | 3 | 0 |
| 3      | 1            | 9 | 0 | 7              | 3 | 0 | 7             | 3 | 0 |
| 4      | 8            | 2 | 0 | 8              | 2 | 0 | 8             | 2 | 0 |
| 5      | 4            | 6 | 0 | 7              | 3 | 0 | 7             | 3 | 0 |

**Table 4.** Failure mode of Panavia F 2.0

| Group* | Thermocycles |   |   |                |   |   |
|--------|--------------|---|---|----------------|---|---|
|        | 0 cycles     |   |   | 10, 000 cycles |   |   |
|        | A            | M | C | A              | M | C |
| 1      | 8            | 2 | 0 | 10             | 0 | 0 |
| 2      | 10           | 0 | 0 | 7              | 3 | 0 |
| 3      | 6            | 4 | 0 | 7              | 3 | 0 |
| 4      | 9            | 1 | 0 | 8              | 2 | 0 |
| 5      | 6            | 4 | 0 | 7              | 3 | 0 |

A: Adhesive failure at the resin-metal interface.

C: Cohesive failure within the resin

M: Mixture of cohesive failure and adhesive failure.

\*Groups:

1: without preparation (abraded with 600-grit silicon-carbide abrasive paper)

2: airborne particle-abraded with 50 mm grain-sized alumina

3: airborne article-abraded with 50 mm grain-sized alumina followed by application of Metalite.

4: airborne particle-abraded with 50 mm grain-sized alumina followed by application of Estenia C&B Opaque Primer.

5: tribochemical silica coating

SD: standard deviation. Identical letters indicate that the values are not statistically different ( $p>0.05$ ).

Significance: Student-Newman-Keuls post hoc grouping

## MANUFACTURERS' DETAILS

- Miro Bright, GC Corp., Tokyo, Japan
- Cristobalite Micro II, GC Corp., Tokyo, Japan
- Kerr Centrifugo casting machine, Kerr Manufacturing Co., Romulus, MI, USA
- Aluminous Powder WA 360, Pana Heraeus Dental Inc., Osaka, Japan
- Micro Blaster, Comco Inc., Burbank, Calif., USA
- Metaltite, Tokuyama Dental Corp., Tokyo, Japan
- Estenia C&B Opaque Primer, Kuraray Medical Inc., Tokyo, Japan
- Rocatec™ junior coating unit, 3M ESPE AG, Seefeld, Germany
- Super-Bond C&B ivory, Sun Medical Co., Ltd., Moriyama, Japan
- Panavia F 2.0, Kuraray Medical Inc., Tokyo, Japan
- Thermal Shock Tester TTS 1, Thomas Kagaku Co., Ltd., Tokyo, Japan
- Autograph AGS-J, Shimadzu Corp., Kyoto, Japan
- STATISTICA for Windows Version 5.5, StatSoft Inc., Tulsa, OK, USA
- Nikon 92052, Nikon Corp., Tokyo, Japan

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