A qualitative analysis of bonding between electroformed surface and veneering ceramics

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Statement of the problem. Recently an innovative method of fabricating indirect restorations by gold electroforming has been developed. But the bond quality and strength of the gold coping to the porcelain is uncertain.
Purpose of study. The purpose of this study is to analyze and evaluate the electroformed gold surface for mechanical bonding between the gold and the ceramic veneering.
Methods/material. Electroformed disks were made using electroforming technique. And the surface of the electroformed coping was analyzed after sandblasting, heat-treatment, bonding agent application, opaque porcelain firing with scanning electron microscopy and energy dispersive x-ray analysis.
Results. In the analysis with SEM, Sandblasting made the sharp edges and undercuts on the electroformed surface, and after bonding agent application, net-like structure were created on the electroformed surface. In the energy dispersive x-ray analysis it is confirmed that electroformed surface contains some impurities.
Conclusion. With the use of sandblasting and bonding agent, electroformed surface seems to be enough to bond with veneering porcelain.

The modern crown fabrication systems with casting procedures, that is conventional technique seems to satisfy most of the requirements in terms of precision. But still, it is said that considerable challenges in investment expansion, metal contraction, and dimensional variations are presented in full ceramic buildup as well as expansion-contraction coefficients[1].

Recently the methods of producing electroformed gold substructures as an alternative to conventional cast metal substructures in the fabrication of porcelain fused to metal restorations were introduced[2].

Electroforming was known to be first introduced in 1838 by Jacobi in Russia[3]. And it was first employed in dentistry in 1856 by Newell[3]. In 1961 O.W. Rogers introduced the use of electroformed gold copings as the core of fixed oral prostheses[4]. He coined the term electroforming to describe the fabrication of gold matrix for a cast gold inlay and later expanded the concept to include gold copings for porcelain crowns. But, the process recommended by Rogers had significant drawbacks. The process used a highly toxic electrolyte that contained potassium cyanide, posing a potential health hazard[2,5]. In the late 1970s Wisman developed an electrolytic system that used a cyanide-free electrolyte, but large expensive equipment was required and the process was rather difficult to perform[5].

In 1991 the Gramm electroforming system (Gramm Technik, Tiefenbronn-Muehlhausen, Germany) was introduced. This system introduced equipment that could fit in a small dental laboratory and the use of a nonhazardous ammonium gold sulfate as the electrolyte solution. The GES system uses 24 karat gold to form copings for use in the production of very precisely fitting crowns, inlays, onlays, telescopic cases and bridges[2,6]. The system produces copings for ceramometal crowns with an even wall thicknesses of 0.2mm and an average marginal gap of 19 microns[6].

Theories of metal-ceramic bonding assume that, an optimal bond between the ceramic and the metal is achieved by means of an oxide film[7]. Because pure gold by itself has no tendency to oxidize, i.e., it offers no means for formations of an optimal bond, another methods should be used for bonding. The manufacturer provides a gold bonding agent. It is known to contain ceramic particles and gold powder.

The purpose of this study is to analyse and evaluate the electroformed gold surface for mechanical bonding between the gold and the ceramic veneering.

MATERIALS AND METHODS

To observe the electroformed surface, electroformed disks were prepared using electroforming techniques as recommended by the manufacturer(Gramm technology). Five cylinders of 5mm in height and 3mm in diameter was fabricated with improved stone(Diekeen, Heraus-Kulzer). A hole was drilled into the lateral aspect of the each cylinder 1mm below the top surface. Then small copper wires were prepared.

The insulation of wires were cut away, exposing the part of the copper wire next to the cylinder. Then they were attached with cyanoacrylate cement. A silver lacquer paint was applied onto the top surface of the stone cylinder. A thin strip of silver lacquer was also used to connect the painted surface to the copper wire.

The cylinders were attached to a plating head and were positioned near the cathode. The electroforming machine used in this study was GAMMAT 21M(Gramm Technlogy, Germany). After gold solution(Ecolyt SG, Gramm, Germany) was measured and poured into the bath, the plating head was lowered into the electrolyte. Correct amount of accelerator was added. The machine timer for the electroforming process and the amount of the gold solution were determined according to the manufacturer's instructions.

After the electroforming process is completed, stone cylinders were cut off and dissolved away from the electroformed disk using a stone removing solution and a ultrasonic cleaner. Finally electroformed disks were produced. Specimens were processed as follows and analyzed with a scanning electron microscope . Energy-dispersive x-ray analysis was also done. Processes on specimens were summarized in table 1.

1. Specimen 1: electroformed disk
2. Specimen 2: electroformed disk was sandblasted with 50 microns aluminum-oxide at 30 psi.
3. Specimen 3: electroformed disk was sand-

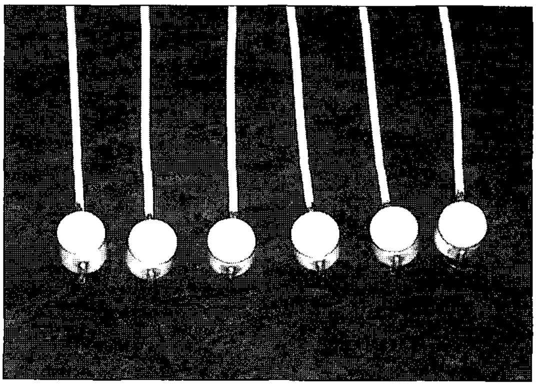

Fig. 1. prepared stone cylinder and copper wire.

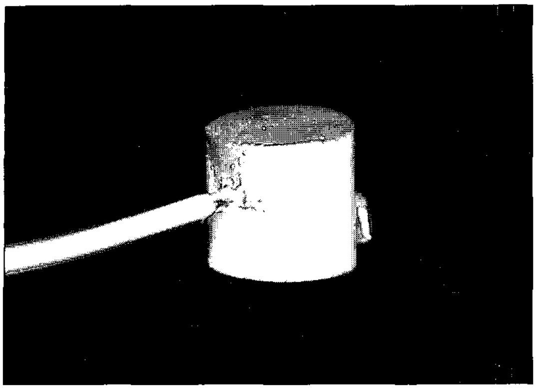

Fig. 2. Applied silver lacquer paint.

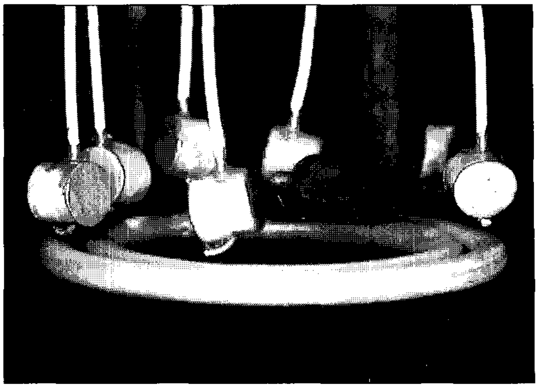

Fig. 3. Finished electroforming process.

blasted. And heat treatment was accomplished. The firing temperature was 950℃.

4. Specimen 4: electroformed disk was sandblasted, a bonding agent was applied, and the disk was fired at 950℃.
5. Specimen 5: electroformed disk was sandblasted, a bonding agent was baked, and opaque porcelain was fired.

Table 1. Processing after the fabrication of electroformed crown.

Specimen	Treatment
1	electroformed disk
2	sandblasting
3	sandblasting, heat treatment
4	sandblasting, bonder
5	sandblasting, bonder, opaque porcelain

RESULTS

In the specimen 1, Scanning electron micrograph image at 5000 magnifications was observed. Slightly uneven, but mostly uniform scale-like structures were observed. The surface was composed of about 1 μm diameter round nodule-like structure. In energy-dispersive x-ray analysis gold, copper, and Carbon were found. Figure 4 shows the surface of electroformed disk and figure 5 shows energy-dispersive x-ray analysis.

In the specimen 2, sandblasted with 50 μm aluminum oxide particles, surface changes was detected at 5000 magnifications. sharp edges and undercuts was observed. Irregular surface is composed of prominences and depressions. In energy-dispersive x-ray analysis gold, aluminum, copper, carbon and oxygen were found. Figure 6 shows the sandblasted surface of electroformed disk and figure 7 shows energy-dispersive x-ray analysis.

In the specimen 3, a roughened surface similar to that of specimen 2 was observed at 5000 magnifications. There were also prominences and depressions, sharp edges, and undercuts. But slight smoothing of the irregularities was observed. In energy-dispersive x-ray analysis, gold, aluminum, and oxygen were found. Figure 8 shows the heat treated and sandblasted surface of electroformed disk and figure 9 shows energy-dispersive x-ray analysis.

In the specimen 4, in which bonding agent was applied after sandblasting, net-like structure was observed at 5000 magnifications. Sharp structures disappeared and layers of fused round nodules were found. In energy-dispersive x-ray analysis only gold could be found. Figure 10 shows the applied bonding agent on electroformed disk and figure 11 shows energy-dispersive x-ray analysis.

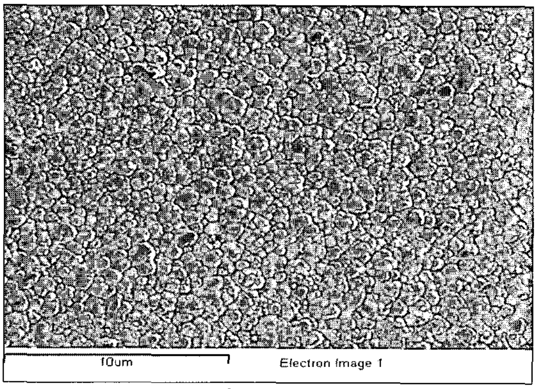

Fig. 4. Specimen 1, the surface of electroformed disk. SEM $\times 5000$.

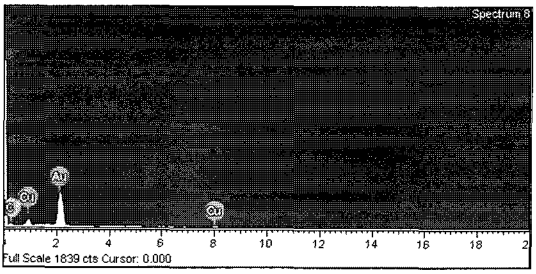

Fig. 5. Energy-dispersive x-ray analysis of the specimen 1.

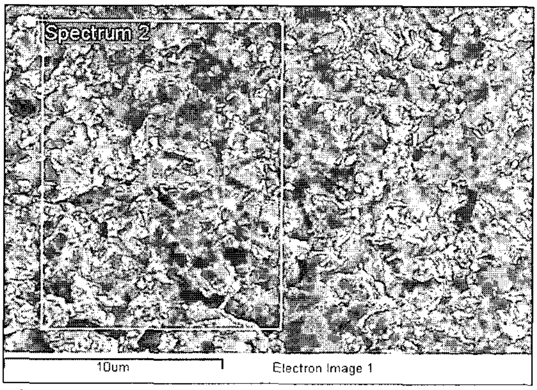

Fig. 6. Specimen 2, sandblasted surface. SEM $\times 5000$.

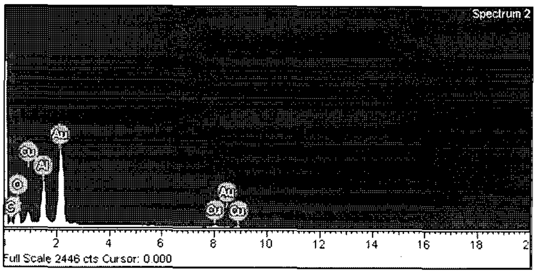

Fig. 7. Energy-dispersive x-ray analysis of the specimen 2.

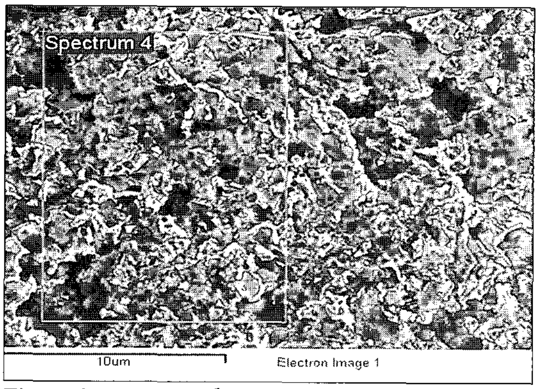

Fig. 8. Specimen 3, heat treated and sandblasted suface of electroformed disk. SEM $\times 5000$.

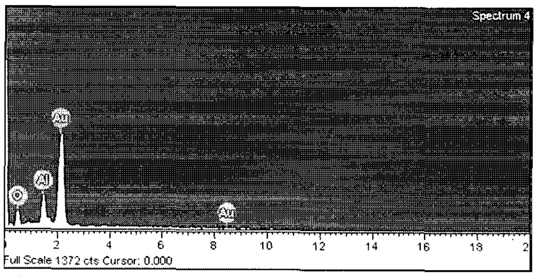

Fig. 9. Energy-dispersive x-ray analysis of the specimen 3.

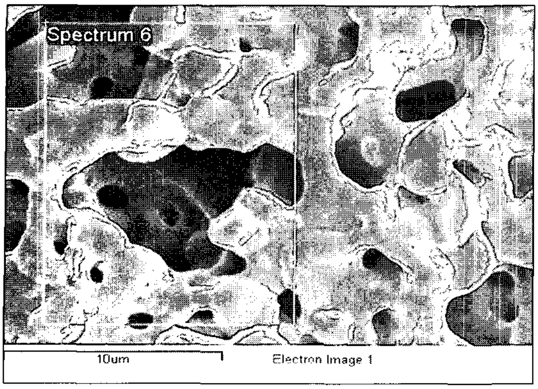

Fig. 10. Specimen 4, applied bonding agent on electroformed disk. SEM ×5000.

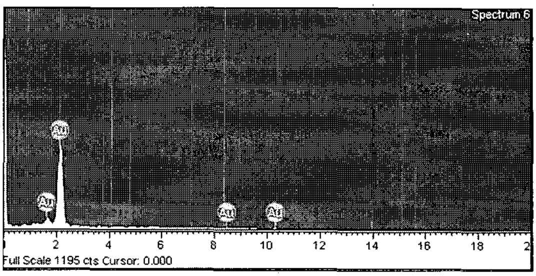

Fig. 11. Energy-dispersive x-ray analysis of the specimen 4.

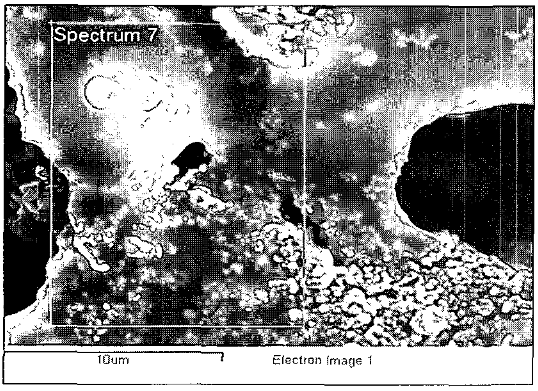

Fig. 12. Specimen 5, opaque porcelain on electroformed surface. SEM ×5000.

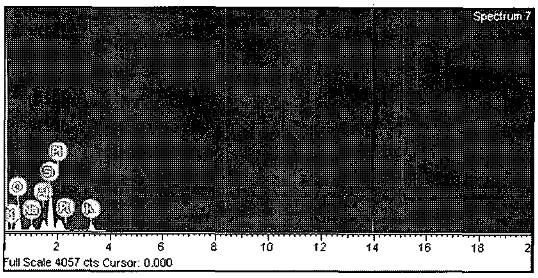

Fig. 13. Energy-dispersive x-ray analysis of the specimen 5.

In the specimen 5, in which opaque firing was done after the applying of a bonding agent, large net-like structure with rough surface was observed. In energy-dispersive x-ray analysis, platinum, potassium, aluminum, natrium, oxygen, and silicone were found. Figure 12 shows the opaque porcelain on electroformed disk and figure 13 shows energy-dispersive x-ray analysis.

DISCUSSIONS

A strong bond between metal and porcelain is known to be essential for the strength of the metal-ceramic system[8]. Knap et al classified bonding mechanisms joining metallic and ceramic materials as mechanical bonds, chemical bonds, and van der Waal's forces[9]. Yamamoto classified bonding mechanisms into several groups: mechanical, chemical, dendritial, transition phase, and van der Waals's forces[8]. Vickery insisted that major attachment force in porcelain-gold prostheses without an intervening bonding agent is derived from compression forces generated by differences in thermal expansion of the two phases[16].

Mechanical bond is an interlocking bond on the interface between metal and glass. That is, the principle of this bonding mechanism is interdigitation between metal and ceramic[7,10]. To get this kind of bond, metal surface is roughened through grinding or sandblasting[7]. Roughening strengthens the bonding effect by enlarging the effective bonding surface, improving wettability and creating undercut areas[7]. In addition, sandblasting also cleans the surface through abrasion, improves wettability by changing surface energy and alters the surface composition through localized fusions[7]. If molten porcelain is wettable on metal, they make close contact with each other and thus molten porcelain may flow easily into fine depressions on metal surfaces, resulting in strong mechanical interlocking after solidification of the porcelain[8].

The chemical bond results from the fact that metal and glass facing each other at a fusion interface hold electrons in common to produce a bonding force[8]. Chemical bond includes atomic bonds, polar bonds, and metallic bonds[7]. The bond between metal and ceramic in conventional casting system is achieved through the oxides found in the boundary layer on the surface of both substances. Observations of precious metal alloys have shown that the base metal components accumulate on the surface of the metal and form strongly adhering oxide layers there, which are bound via their metal ions in the alloy lattice. During firing these oxides enter into a bond with the silica network of the ceramic. This causes a bond to the silicon dioxide of the ceramic, similar to an oxygen bridge bond[7].

Van der Waals forces refers to a bond by means of an electrostatic attraction between two atoms that approach each other within a space in which no chemical bond is effective[8]. Van der Waals forces are achieved through dipole formation[11]. Van der Waals forces are known to achieve little direct influence on the bonding strength but are important because of their ability to improve the surface wetting of a metal through the viscous ceramic material during firing. The bond created by Van der Waals force is known not to be dependent on the presence of an oxide layer. Sufficient wetting of the surface plays a role in making Van der Waals forces. In electoforming system oxide layer does not exist, so Van der Waals forces probably plays a role in bonding between gold and porcelain.

In specimen 1, evenly round, scale-like structure was observed. In EDX(Energey-dispersive x-ray) analysis gold, copper, and carbon was found. Electroformed coping is said to be made of 24karat gold[2], but in this study the existence of impurities were confirmed. This contamination probably resulted from the processes during which specimens were fabricated. Contact with copper wire was thought to be possible cause and gold solution, Ecolyt SG itself might contain impurities.

In electroforming system, the mechanical bond can be increased by sandblasting or application of a bonding agent. In specimen 2, roughened surface was observed. These surface is expected to attribute to the mechanical retention. In EDX analysis of specimen 2, in addition to gold, copper, oxygen and aluminum were found. Oxygen and aluminum were thought to be resulted from sandblasting and copper was thought to be impurities. During making specimens every effort was done for the prevention of contamination. But, there seemed to be some contamination.

In specimen 3, heating the electroformed disk was done. In conventional ceramometal system, the purpose of heating is to make small amounts of additive element diffuse to and precipitate on the alloy surface to form their oxide films which will take an important part in bonding with porcelain[8]. But in this study, none of the element such as Sn, In, and Fe were expected to appear as a result of heating, because gold electroformed disk is made of pure gold. In EDX analysis of specimen 3, gold, aluminum, and oxygen could be found as expected. Besides making oxide layer, heating is known to be effective to decrease bubbles at the interface to a considerable degree. One of the reason why heating decreases interfacial bubbles is reduction of roughness on the interfacial metal surface. Yamamoto said that after heating the surface change is great enough to be visible to the naked eye and it may be resulted from sagging. But in specimen 3, although a slight smoothing of the surface was observed, the structures similar to the ones before heat treatment were observed.

In electroforming system, 24 carat gold does not create any oxide layer. Instead of using the conventional oxide firing cycle, a bonding agent is applied. In specimen 4, gold bonder was applied on the surface of electroformed disk. The bonder is a paste composed of gold and ceramic particles. After firing at 950℃, the fusion of gold particles were observed. As a result of the fusion of gold particles, net-like layers were formed. These structures seems to be enough to provide mechanical retention for ceramic-metal bonding. In EDX analysis of specimen 4, only gold was found. Manufacturer said that the ceramic particle, deposited in the upper third of the bonding layer, will create a reliable bond with the ceramic material that will be applied afterwards[13]. According to manufacturer, bonder is composed of 99.99% of gold and ceramic particles are small in quantity. So in this study ceramic particles might be buried in gold or might not be included in observation field.

In specimen 5, ceramic surface covering gold surface was found. In EDX analysis gold was not detected and the elements of the feldspathic porcelain like potassium were found.

In the fields of conventional ceramometal system, a lot of studies was made, but despite *numerous investigations, it is said that the exact* nature of the bond has not been defined[14]. And some authors said that the strength of porcelain metal bond has been questioned[15] and studies need to be conducted to measure its strength[12]. In this study the electroformed surfaces after sandblasting and bonding agent application were observed. This study examined only one aspect necessary for adequate bonding between gold and porcelain. The strength and the nature of the interface between gold and porcelain need to be measured quantitively.

CONCLUSION

Although the bonder layer and the sandblasted layer of the electroformed surface were analyzed in this study, there is limited data on the nature and strength of the bond between the gold and the porcelain. As some authors[3,15] pointed out, the bond quality and strength of the gold surface to the porcelain need to be further investigated.

With scanning electron microscopy and energy dispersive x-ray analysis, following results were observed and inferred.

1. In the surface analysis with scanning electron microscopy the retention forms sandblasting created on the electroformed surface was confirmed.
2. In the surface analysis with scanning electron microscopy it is confirmed that bonding agent makes sufficient retention forms on the electroformed surface.
3. In the energy dispersive x-ray analysis, the existence of impurities on the electroformed surface was observed.

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