Mechanism by which Porous Structure is Formed on the Surface of Gold Alloy Containing Only Cu as Base Metal

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Received June 6, 2005/Accepted September 6, 2005

Gold alloys with Cu contents of 10 mass%, 20%, and 30% were used for morphological observation of porous surface structures after heating at 800°C in air followed by pickling with acid solution. With increasing Cu content in the gold alloy, the internal oxidation zone became well-developed in the alloy matrix. The mechanism by which a porous structure was formed on the surface of a gold alloy containing only Cu as a base metal was thought to be as follows: Cu₂O which formed along the grain boundaries acted as a diffusion path, permitting the penetration of O²⁻ into the inner alloy matrix, and thereby resulting in internal oxidation occurring predominantly along the grain boundaries.

Key words: High-temperature oxidation, Gold alloy, Copper oxide, Pickling, Porous structure, Resin bonding

INTRODUCTION

In dental noble metal alloys containing Cu, external and internal oxidation zones - which composed of Cu oxides, CuO and/or Cu₂O - were formed on the alloy surface by heating at a high temperature in air. A porous structure was formed on the alloy surface after removing the internal oxidation particles with an acid solution. It was thought that this porous structure would enhance mechanical bonding with dental adhesive resin. We investigated the bonding of 4-META resins to a porous 14K gold alloy surface created by high-temperature oxidation treatment and subsequent pickling to examine the effects of mechanical and chemical factors on bond strength.

In previous studies, the morphology of the internal oxidation zone of dental gold alloys was found to change markedly according to the kind of base metal in the composition: Ni, In, or Cr with Cu. In 14K gold alloy containing 24 mass% Cu, the external oxidation zone and internal oxidation particles - which composed of copper oxide - were removed by pickling in a thioglycolic acid solution, resulting in the formation of a porous alloy surface. However, NiO, In₂O₃, and Cr₂O₃ with Cu oxide in the internal oxidation zone could not be removed from other oxidized gold alloys by pickling - they remained in the alloy matrix near the surface because the internal oxides were well-developed and fine needle-like in shape. This suggests that a gold alloy containing only Cu as a base metal is a suitable alloy for forming interconnected internal oxide deposits, resulting in the formation of a porous structure on the alloy surface after pickling.

The purpose of this study was to investigate the effects of Cu content (in gold alloys) and heating time on the porous structure, which enhances mechanical bonding with dental adhesive resin. Although bonding of dental adhesive resin with dental alloys has been extensively studied, there are no reports with respect to the improvement of bonding strength between dental adhesive resin and dental gold alloy by the mechanical retention method described in the present paper.

MATERIALS AND METHODS

Table 1 shows the compositions of the gold alloys used in the present study. The alloys contained Au, Pt, Pd, and Ag as a precious metal and Cu as a base metal. The Cu content was changed in the range of 10 mass% to 30% with decreasing Au amount. The metals, more than 99.99% pure, were weighed to give a 30-g alloy sample and then melted in an argon atmosphere. Melting was done in an alumina crucible covered with a graphite tube using a high-frequency induction furnace. Weight loss during melting was less than 0.01%.

The alloys were cast in 3 mm × 3 mm × 10 mm ingots to prepare specimens for morphological observation of the oxidation zones by SEM. Cast specimens were polished metallographically to a mirror-like finish using silicon carbide paper ( # 240, # 400, and # 600) followed by alumina paste (3 μm and 0.05 μm), and then oxidized at 800°C in air in a clean
electric furnace. Oxidized specimens were subsequently pickled in a thioglycolic acid solution to remove the external and internal oxides on the alloy surface, washed in an ultrasonic bath with distilled water, and dried in a current of air. The oxidized specimens were mounted with the use of a hard resin (Epomet, Buehler, Lake Bluff, IL) to prevent the edges from becoming rounded during polishing. For the pickled specimens, 4-META resin was first applied to the porous surface and then the specimens were mounted with the hard resin. Two kinds of cross section, perpendicular and inclined 45° to the oxidized surface, were polished metallographically as described previously.

A carbon film of 30-40 nm in thickness was deposited on the polished alloy surface to provide electrical conductivity for observation by a scanning electron microscope (X-650, Hitachi, Tokyo, Japan).

RESULTS

The images shown in Fig. 1 are SEM images perpendicular to the oxidized surfaces of gold alloys after oxidizing at 800°C in air for one hour — namely Alloy No. 1 (Fig. 1(a)), Alloy No. 2 (Fig. 1(b)), and Alloy No. 3 (Fig. 1(c)). An external oxidation zone was formed on the alloy surface, and internal oxidation particles composed of copper oxide precipitated in the alloy matrix from the alloy surface. Thicknesses of the external and internal oxidation layers increased with increasing Cu content.

Fig. 2 shows the SEM images of the porous surface structure after pickling. The surface structure was made more porous with increasing Cu content.

Fig. 3 shows the SEM images of cross sections inclined 45° to the oxidized surface obtained from different Cu content gold alloys, Alloy No. 1 (Fig. 3(a)), Alloy No. 2 (Fig. 3(b)), and Alloy No. 3 (Fig. 3(c)), heated at 800°C in air for one hour and then subjected to pickling followed by 4-META resin bonding. The inclined cross sections revealed clearly that the internal oxidation particles were connected three-dimensionally, although the inner oxide particles were isolated two-dimensionally in the perpendicular cross sections of Fig. 1. Characteristic Cu Kα X-ray images showed that the external and internal oxidation particles were almost completely removed by pickling except for the deeper portion of Alloy No. 3. As shown in Fig. 3(c), inner oxide particles in the deeper portion were not removed with the thioglycolic acid solution. Further, SEM and X-ray images showed that resin had impregnated the inter-

![Fig. 1](image1.png) Cross sections perpendicular to oxidized surfaces of gold alloys with Cu content at (a) 10 mass%; (b) 20%; and (c) 30% after heating at 800°C in air for 1 hr.

![Fig. 2](image2.png) Surfaces of gold alloys with Cu content at (a) 10 mass%; (b) 20%; and (c) 30% after heating at 800°C in air for 1 hr, followed by pickling.
Fig. 3 Cross sections inclined 45° to the oxidized surfaces of gold alloys with Cu content at (a) 10 mass%; (b) 20%; and (c) 30% after heating at 800°C in air for 1 hr, pickling with acid solution, and bonding with 4-META resin.

Fig. 4 Porous structures after pickling on surfaces of gold alloy containing 30 mass% Cu that had been heated at 800°C in air (a) for 1 hr, and (b) for 10 hr.

Fig. 5 Schematic representations of the growth of an external oxidation zone (CuO) and internal oxidation zone (Cu₂O) — namely as-polished surface (Fig. 5(a)), after heating for a short time or a gold alloy with low Cu content (Fig. 5(b)), and after heating for long time or a gold alloy with high Cu content (Fig. 5(c)). Likewise, Fig. 4(b) shows the enlarged pore sizes after prolonged heating time.

DISCUSSION
Mechanism of the formation of porous structure on alloy surface
In a previous study, it was shown that the oxidation zone of a dental 14K gold alloy containing Cu formed after high-temperature oxidation by heating at 800°C in air. Through characteristic X-ray images and state analysis by electron probe microanalysis, it was found that the external oxidation zone was composed of two copper oxide layers — an outer layer of CuO and an inner layer of Cu₂O, and that the internal oxide particles were composed of Cu₂O only.

The shape and distribution of the internal oxidation particles depend not only on the kind and amount of base metal, but also on various other factors including oxidation temperature, heating time, oxygen pressure, grain size of alloy, and extent of grain growth during heat treatment. Fig. 5 shows the schematic representations of the growth of an external oxidation zone (CuO) and internal oxidation zone (Cu₂O) — namely as-polished surface (Fig. 5(a)), after heating for a short time or a gold alloy with low Cu content (Fig. 5(b)), and after heating for long time or a gold alloy with high Cu content (Fig. 5(c)). Likewise, Fig. 4(b) shows the enlarged pore sizes after prolonged heating time.

Meijering reported three conditions for internal oxidation of a solute B in a binary alloy A-B: (1) oxygen must have appreciable solubility in the alloy; (2) oxygen must diffuse more rapidly in solvent A than in solute B; and (3) the oxygen affinity of element B must be considerably greater than that of element A. The gold alloys investigated here did not satisfy the first and third requirements because the solubility of oxygen is very small in a gold alloy.
Therefore, it might be concluded that the mechanism of internal oxidation of the gold alloy in this study was essentially different from the oxidation that satisfies the above three conditions.

Fig. 6 shows the formation mechanism of a porous structure by high-temperature oxidation on a gold alloy surface containing only Cu as a base metal. Oxygen must be appreciably soluble in an alloy in order for internal oxidation of an alloying element to occur. Since the solubility of oxygen in gold is very low, the gold alloys used in the present study did not satisfy this condition for internal oxidation. However, oxide precipitation has been observed at the grain boundaries in gold alloys. The oxide, which forms along the grain boundaries, acts as a diffusion path that permits the penetration of O$_2^-$ into the bulk alloy matrix, resulting in internal oxidation predominantly along the grain boundaries.

In the present study, the Cu$_2$O which formed along the grain boundaries acted as the diffusion path, thereby permitting the penetration of O$_2^-$ into the inner alloy matrix. Cu$_2$O formed at the interface of CuO and alloy matrix. The Cu content at the interface of the alloy matrix was reduced by the formation of Cu$_2$O. As a result, Cu atoms diffused to the oxide-alloy interface from the alloy matrix with a concentration gradient of Cu in the alloy matrix. Internal oxidation occurs predominantly along the grain boundaries following high-temperature oxidation. It was found that with increasing Cu content in the gold alloy, the internal oxidation zone became well-developed on the alloy surface. After removing the external and internal oxidation zones composed of copper oxides by pickling, a porous structure was formed on the gold alloy surface.

**Bond strength with dental adhesive resin and porous surface**

In a previous study, SEM observation showed many resin tags on the resin side of the bond structure after removal of the gold alloy matrix with aqua regia. The bond strength of 4-META resin to the porous alloy surface was 38±3 (mean ± SD) MPa, whereas that to a flat alloy surface with the same composition was 19±1 MPa. The bond strength of a self-cured resin without 4-META to the porous alloy surface was 24±2 MPa.

In the present study, the external and internal oxidation particles were almost completely removed by pickling, although the inner oxide particles in the deeper portion were not removed with the thioglycolic acid solution as shown in Fig. 3(c). Further, SEM and X-ray images showed that resin had impregnated the internal oxidation pores. On this ground, it was thought that the residual inner oxide particles would exert no influence on the bonding.

Fig. 5 Growth of external oxidation zone (CuO) and internal oxidation zone (Cu$_2$O): (a) an as-polished surface; (b) after heating for a short time or low Cu content; and (c) after heating for a long time or high Cu content.

Fig. 6 Mechanism of formation of a porous structure on alloy surface by high-temperature oxidation.
strength of resin. Joints of dental adhesive resin bonded to dental alloys weaken in wet environments, though adhesion is strong in dry environments. One example is the separation or peeling that occurs after long-term use in the oral environment. When water molecules have destroyed the chemical bond, the bond strength is lowered to a level that is sustained chiefly by mechanical retention.

As shown in Fig. 1, each internal oxidation particle was isolated two-dimensionally. But as shown in the 45° inclined cross sections in Fig. 3, the internal oxidation particles were actually connected three-dimensionally with the external oxidation zone. Indeed, the impregnated resin network on the alloy surface might seem to enhance the mechanical retention of resin bonding with the gold alloy. Since mechanical bonding played an important role in maintaining the bond structure in this situation, increased mechanical retention was essential for the durability of the adhesion interface.

The surface structure was made more porous by increasing the Cu content, suggesting that a stronger mechanical bonding could be expected. On this note, further research on bonding strength of gold alloys with different Cu contents is needed.

CONCLUSIONS
We have reported that a gold alloy containing only Cu as a base metal is a suitable alloy for forming interconnected internal oxide deposits, resulting in the formation of a porous structure on the oxidized alloy surface after pickling. The effect of Cu content in a gold alloy on internal oxide particles was investigated in the present study: gold alloys with Cu contents of 10 mass%, 20%, and 30% were used for morphological observation of porous surface structures after heating at 800°C in air followed by pickling.

With increasing Cu content in the gold alloy, the internal oxidation zone became well-developed in the alloy matrix. The mechanism by which a porous structure was formed on the surface of a gold alloy containing only Cu as a base metal was thought to be as follows: Cu2O which formed along the grain boundaries acted as a diffusion path, permitting the penetration of O2− into the inner alloy matrix, and thereby resulting in internal oxidation occurring predominantly along the grain boundaries. It is speculated that the pores formed by dissolution of the internal oxidation particles with acid solution helped to increase mechanical retention and establish a reliable bonding. However, the resistance of gold alloys to corrosion and tarnish decreases with increase in Cu content. Therefore, the optimal Cu content should be further addressed in order to develop a gold alloy favorable for resin bonding, on which a porous structure can be formed without reducing corrosion and tarnish resistance.

ACKNOWLEDGEMENTS
This work was supported by a Grant-in-aid for Scientific Research (B) from the Ministry of Education, Culture, Sports, Science, and Technology of Japan and also partially by GC Corporation.

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