

Age-Hardening Behavior and Structural Changes in a Commercial Dental Au-Ag-Cu-Pd Alloy

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=Abstract=

The age-hardening behavior and the structural changes in a commercial dental Au-Ag-Cu-Pd alloy were investigated by means of hardness test, optical and scanning electron microscopic observation, energy dispersive spectroscopy and X-ray diffraction study.

The drastic reduction in hardness by prolonged aging occurred after a rapid increase in hardness at the initial stage by the isothermal aging at 350 °C. This softening was due to the broad precipitates formation of the lamellar structure which was composed of the f.c.t. AuCu I ordered f.c.t. phase containing Pd and the f.c.c. Ag-rich α_1 solid solution f.c.c. phase containing Au.

Key words : Gold alloy, Age-hardening, Overaging, Lamellar structure

INTRODUCTION

Dental casting gold alloys are essentially ternary alloys of gold, copper and silver with small amounts of other elements, and should contain gold and platinum-group metals of more than 75 wt. % according to American dental association specification No. 5. Many of the dental gold alloys exhibit obvious age-hardening characteristics, and their hardening mechanisms and microstructures are well known.

Alternative low-gold dental alloys which are available commercially are widely used. Their gold content is below previously accepted minimal level. Therefore, these alloys contain palladium to preserve the tarnish and corrosion resistance.

There are many studies on the age-hardening mechanisms and the microstructures in commercial dental Au-Ag-Cu-Pd alloys¹⁻⁷⁾. Nevertheless, there is no sufficient information concerning these commercial dental gold alloys, and the age-hardening behaviors and the structural chan-

ges in these alloys have not been completely elucidated.

Therefore, the present study attempted to elucidate the age-hardening behavior and the structural changes in a commercial dental Au-Ag-Cu-Pd alloy. The relationship between the age-hardening behavior and the structural features was investigated by means of hardness test, optical and scanning electron microscopic observations, energy dispersive spectroscopy and X-ray diffraction study.

MATERIALS and METHODS

The specimen alloy used in the present study was a commercial dental gold alloy (Duallor G Alloy, Degussa, Germany). The nominal composition of the alloy is given in Table 1.

Sheets supplied by manufacturer were used for hardness measurements, optical and scanning electron microscopic observations, energy dispersive spectroscopy. Powder specimens for X-ray diffraction study were obtained by filing the alloy. All specimens were annealed at 800 °C for 30 min

Table 1. Chemical composition of the alloy used

nominal	Au	Ag	Cu	Pd	Zn	Ir
wt. %	55.0	25.0	11.6	7.9	≤2	≤2
at. %	36.4	30.2	23.8	9.7		

to acquire a single phase of solid solution and then quenched into iced brine, and were subjected to heat treatment at required temperatures for required periods in a molten salt bath and then quenched into iced brine.

The specimens for hardness measurements were isochronally aged in a 200~500 °C range for 10, 20, 50 min, and were isothermally aged for various periods up to 20000 min at 350 °C corresponding to the temperature of the hardness peak in the isochronal age-hardening curves. The microhardness measurements were made on the solution-treated specimen and the aged specimens using a diamond pyramid hardness indenter (Shimadzu Co., HMV-2000, Japan) with a 300gf load and a 10 sec holding time.

The specimens for optical and scanning electron microscopic observations, energy dispersive spectroscopy were aged at 350 °C for required periods, and were prepared using a standard metallographic technique. A freshly prepared aqueous solution of 10% potassium cyanide and 10% ammonium persulfate was utilized for the final etching of the samples. Scanning electron microscope used was Scanning microscope (JEOL, JSM-5400, Japan) equipped with Energy-dispersive system (NORAN, 648B-1SSS, USA) operating at 20 kV.

The powder specimen for X-ray diffraction study was vacuum-sealed in a silica tube, and was solution-treated at 800 °C for 30 min and aged at 350 °C for 20000 min to obtain stable phase. The diffracton equipment used was X-ray diffractometer system (Rigaku, 2013, Japan) operating at 40 kV and 30 mA and Cu α radiation with Ni-filters.

RESULTS

Isochronal age-hardening curves of the test alloy are shown in Fig. 1. The results of the isochronal aging in a 200~500 °C range for 10~50 min show similar curves. The hardness increases progressively from the value of 159

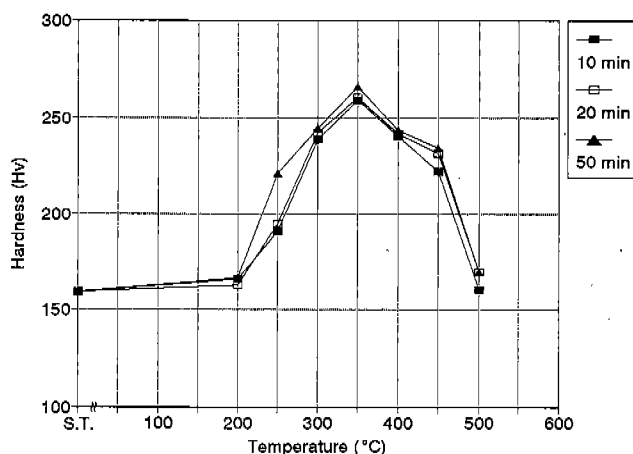


Fig. 1. Isochronal age-hardening curves for 10, 20, 50 min.

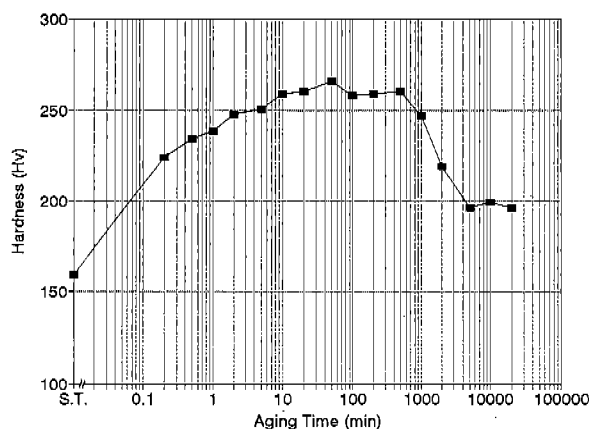


Fig. 2. Isothermal age-hardening curve at 350 °C.

VHN in the solution-treated specimen to the hardness peak of 259~266 VHN in the specimen aged at 350 °C for 10~50 min, and decreases progressively with raising the aging temperature above 350 °C. This implies the temperature, 350 °C is most effective for the age-hardening of this alloy.

Isothermal age-hardening curve at 350 °C of the test alloy is shown in Fig. 2. By the isothermal aging at 350 °C corresponding to the temperature of the hardness peaks in the isochronal age-hardening curves, initially the specimen acts with a rapid increase in hardness, and then maintains a slower increase and a relatively higher hardness value in the early stage of aging. A drastic decrease in hardness, however, was found after 5000 min aging. This softening, namely overaging, occur following prolonged aging.

Optical micrographs of the specimens are shown in Fig. 3. Fig. 3(A) is a optical micrograph obtained from the specimen solution-treated at 800 °C for 30 min to acquire a single phase of solid solution. The microstructure of solution treated specimen was homogeneous equiaxed structure.

Fig. 3(B)~(F) are optical micrographs obtained from the specimen aged at 350 °C for 10 min, 500 min, 2000 min, 5000 min, 20000 min respectively. By the isothermal aging at 350 °C, precipitates were appeared after 10 min aging, and were formed predominantly along the grain boundaries initially and developed into the grain interior, and then the area of precipitates structure was broadened following prolonged aging. By lengthy aging, the grain interior were completely covered with precipitates finally. The dimensions of precipitates structure grew with increasing aging time.

The specimen aged at 350 °C for 2000 min where a marked decrease in hardness was observed shows the considerable area of precipitates structure. The marked decrease in hardness, namely overaging with softening seems to coincide with the broadening of precipitates structure in the OM photographs. This implies that precipitates contribute to the softening.

Scanning electron micrographs of the specimens are shown in Fig. 4. A significant difference in microstructure between the original equiaxed structure and the precipitates structure has been confirmed in the SEM photographs. SEM photographs show that precipitates are constructed of distinct lamellar structure. Lamellar structure was formed predominantly along the grain boundary in the early stage of aging. And the micrograph of the specimen aged at 350 °C for 10 min shows well-arranged lamellar structure perpendicular to the grain boundaries alternating regularly.

A continuous growth of the lamellar structure which contributed to the softening occurred following prolonged aging. This means that a single phase of solid solution is transformed into the lamellar structure by aging.

Energy dispersive spectroscopy was made to confirm the distribution of each of four elements in the lamellar structure. Fig. 5 shows a SEM photograph of specimen aged for 20000 min and EDS profiles taken from the same area as the SEM photograph. EDS profiles demonstrate that

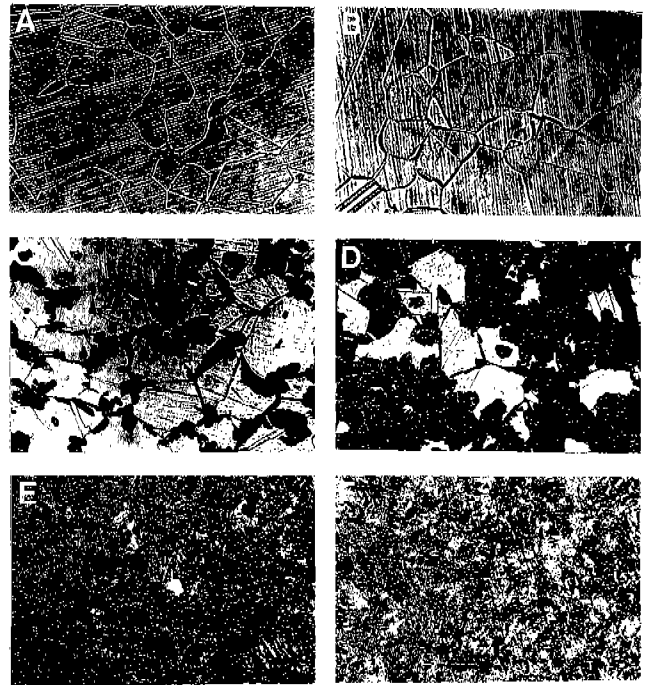


Fig. 3. Optical micrographs($\times 400$) of the specimens solution-treated at 800 °C for 30 min (A), and aged at 350 °C for 10 min (B), 500 min (C), 2000 min (D), 5000 min (E), 20000 min (F).

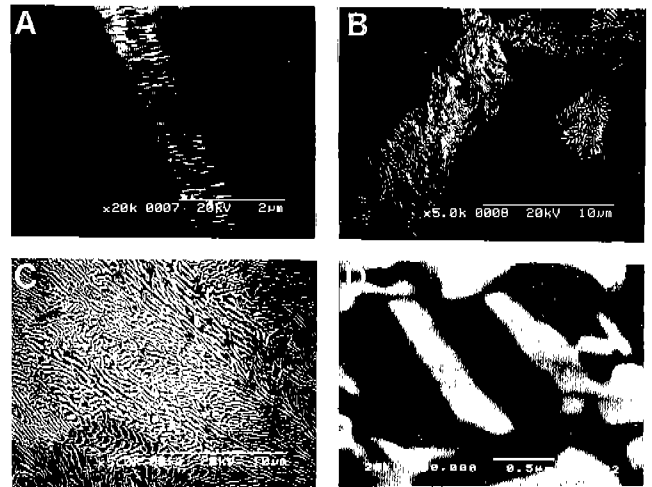


Fig. 4. Scanning electron micrographs of the specimens aged at 350 °C for 10 min (A: $\times 20000$), 500 min (B: $\times 5000$), 20000 min (C: $\times 5000$, D: $\times 50000$).

two distinct layers of lamellar structure are silver-rich, and copper-and-palladium-rich respectively, and that gold is dis-

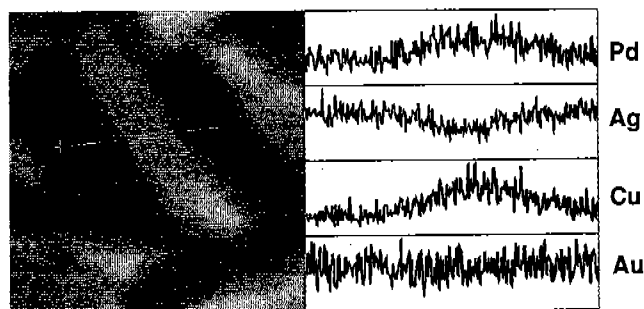


Fig. 5. EDS profiles of the specimen aged at 350°C for 20000 min.

tributed evenly.

X-ray diffraction study on the specimens solution-treated at 800°C for 30 min and aged at 350°C for 20000 min was performed to identify the stable phase of the alloy. The single phase of α solid solution at 800°C, and the co-existence of the AuCu I ordered phase and the silver-rich α_1 phase at 350°C were confirmed by X-ray diffraction analysis.

Therefore it can be thought that α single phase of the solution-treated specimen is transformed into the co-existence of the AuCu I ordered phase, with a f.c.t. structure and the silver-rich α_1 phase, with a f.c.c. structure by aging at 350°C.

DISCUSSION

The isothermal age-hardening curve of the present alloy demonstrated the drastic reduction in hardness by prolonged aging after showing a rapid increase in hardness at the initial stage of aging as seen in Figure 2. This initial increase in hardness was observed before structural change was produced. Accordingly, some changes in the grain interior are assumed. Yasuda et al⁴⁾, reported that the initial hardening in the alloy (39.8 at. % Au-27.4 at. % Ag-25.3 at. % Cu-7.6 at. % Pd), which had a composition similar to that employed in the present study, was due to the introduction of coherency strain at the interface between the metastable AuCu I' ordered phase and the matrix, and the grain boundary precipitates did not contribute to the age-hardening. And the age-hardening in the alloy (16.4 at. % Au-29.0 at. % Ag-30.6 at. % Cu-22.3 at. % Pd-1.7 at.

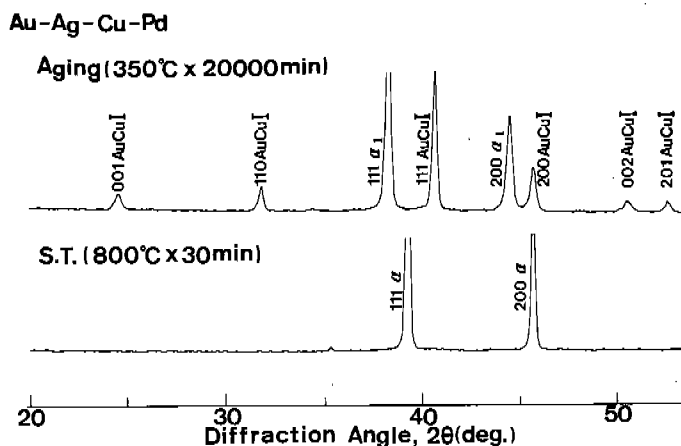


Fig. 6. X-ray diffraction patterns of the specimen solution-treated at 800°C for 30 min and aged at 350°C for 20000 min.

% Zn) was considered to be generated by the coherency strain developed between the AuCu I' structure and the matrix, which was reported by Hisatsune et al²⁾.

The marked decrease in hardness (Fig. 2) coincides with the broadening of precipitates structure in the OM photographs (Fig. 3). Namely, the overaging with softening was attributed to the formation and continuous growth of the precipitates by the aging of the supersaturated solid solution in the present alloy. And precipitates were composed of a lamellar structure (Fig. 4). It was suggested that the nodule formation at the grain boundary by the aging of the alloy (11.2 at. % Au-45.8 at. % Ag-17.1 at. % Cu-26.0 at. % Pd) corresponded to overaging¹⁾. Hisatsune et al²⁾ reported that on prolonged aging in the alloy which they used the formation of a nodular structure at the grain boundaries produced softening, and it was inferred that the formation of the stable phase nodule produces stress relaxation at the grain boundaries. According to Udoh et al⁵⁾, the mechanism of the overaging in the alloy (39.8 at. % Au-27.4 at. % Ag-25.3 at. % Cu-7.6 at. % Pd) was interpreted as the loss of coherency at the interfaces of the adjacent lamellae which consists of the equilibrium AuCu I ordered phase and the silver-rich solid solution phase.

The microstructural changes in the present alloy at 300°C are analogous to those in the alloy (16.4 at. % Au-29.0 at. % Ag-30.6 at. % Cu-22.3 at. % Pd-1.7 at. % Zn) at 300°C which were reported by Hisatsune et al^{2, 3)}, except

for the difference of the phases formed. In the present alloy, two distinguishable phases, the AuCu I ordered phase and the silver-rich α_1 phase which were formed by prolonging the aging time were identified by means of X-ray diffraction study. This result coincides with reports by Yasuda et al⁴⁾ and Udoh et al⁵⁾, although the composition of the alloy used in this study is slightly different from the alloys that they used. They reported that prolonging the aging time caused the formation of a lamellar structure which consisted of the equilibrium AuCu I ordered phase and the silver-rich solid solution phase.

Fig. 7 presents the suggested isothermal sections of Au-Cu-Ag ternary phase diagram at 300°C and 350°C⁸⁾. The hatched triangles indicate the compositional boundary of the present alloy. The compositional boundary exists mainly in the co-existence region of the silver-rich α_1 phase and the AuCu II ordered phase at 300°C, and exists in the co-existence region of α_1 phase and α_2 phase, or the silver-rich α_1 phase and the AuCu II ordered phase at 350°C.

There is general agreement between the suggested isothermal section of Au-Cu-Ag ternary phase diagram and the EDS profiles of the present alloy shown in Fig. 5. As shown in Fig. 7, the tie lines are nearly parallel to the Ag-Cu binary edge within the compositional range of the present alloy, therefore the 2-phase separation with the even distribution of gold could occur. EDS profiles demonstrated that two alternating layers of the lamellar structure were Ag-Au rich and Au-Cu-Pd rich respectively, although the exact phase of lamellar structure could not be determined from the EDS profiles unfortunately.

The result of the X-ray diffraction study on the present alloy does not agree with the 350°C isothermal section of Au-Cu-Ag ternary phase diagram. The stable phase of the present alloy at 350°C was the co-existence of the AuCu I ordered phase and the Ag-rich α_1 phase as shown in Fig. 6.

From the results of EDS profiles and X-ray diffraction patterns, it could be thought that the stable phase of the present alloy at 350°C is the co-existence of the AuCu ordered phase containing palladium and the Ag-rich α_1 phase containing gold, and that the transition temperature of AuCu ordered structure is raised with the addition of palladium^{9, 10)}. Thus, it was concluded that the lamellar

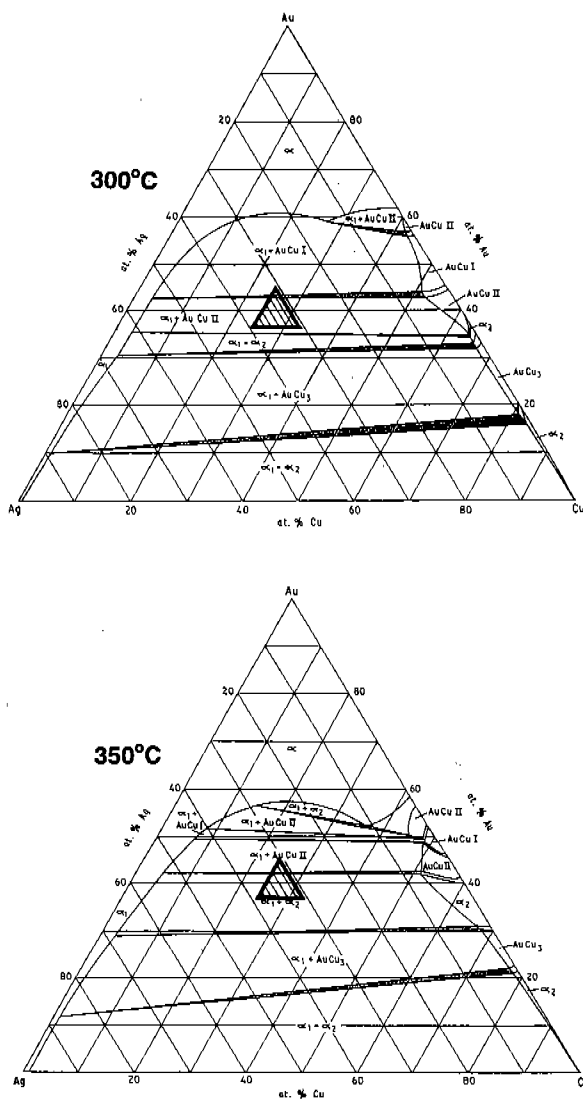


Fig. 7. Suggested isothermal sections of Au-Cu-Ag ternary phase diagram at 300°C and 350°C. The hatched triangles show the compositional boundary of this alloy.

structure consists of the AuCu I ordered phase containing palladium and the Ag-rich α_1 solid solution phase containing gold.

CONCLUSION

The age-hardening behavior and the structural changes in a commercial dental Au-Ag-Cu-Pd alloy were investigated by means of hardness test, optical and scanning electron microscopic observation, energy dispersive spectroscopy and X-ray diffraction study. The following results

were obtained.

1. The drastic reduction in hardness by prolonged aging occurred after a rapid increase in hardness at the initial stage by the isothermal aging at 350°C.
2. The precipitates constructed of alternating lamellae were formed at the grain boundaries initially and developed into the grain interior by aging.
3. The softening occurred following prolonged aging was attributed to the broad precipitates formation of the lamellar structure which was composed of the f.c.t. AuCu I ordered f.c.t. phase containing palladium and the f.c.c. Ag-rich α_1 solid solution f.c.c. phase containing gold.

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=국문초록=

시판 치과용 Au-Ag-Cu-Pd 합금의 시효경화 거동과 미세조직 변화를 경도시험, 광학현미경 및 주사전자현미경 관찰, 에너지분산 X-선 분광법, X-선회절 실험으로 연구하여 다음과 같은 결과를 얻었다.

용체화처리된 Au-Ag-Cu-Pd 합금은 350°C 등온시효처리에 의해, 경도가 시효초기에 신속히 상승하여 일정한 기간 동안 유지된 후, 급격히 저하하였다.

과시효에 의한 경도의 급격한 감소는 Au를 고용하는 f.c.c.의 Ag-rich α_1 상과 Pd를 고용하는 f.c.t.의 AuCu I형 규칙상의 2상 공존으로 된, 미세한 층상조직의 석출 증가에 기인하였다.