Precipitation Hardening in a Dental Low-gold Alloy

Hyung-II KIM, Young-Hwan PARK, Hee-Kyung LEE, Hyo-Joung SEOL1, Takanobu SHIRAISHI1 and Kunihiro HISATSUNE1
Department of Dental Materials, College of Dentistry, Pusan National University
1-10 Ami-dong, Seo-gu, Pusan 602-739, Korea
1 Division of Dental and Biomedical Materials Science, Graduate School of Biomedical Science, Nagasaki University
1-7-1 Sakamoto, Nagasaki 852-8588, Japan

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Age-hardening characteristics in a dental low-gold alloy composed of 40.0 wt% Au - 35.0 wt% Ag - 7.9 wt% Pd - 7.0 wt% Cu - 5.0 wt% In - 3.5 wt% Zn - 1.5 wt% Sn, were investigated by means of the hardness test, XRD study, SEM observations and EPMA. The following results were obtained.

The age-hardening was characterized by a precipitation of Cu-rich $\alpha_2$ phase in the $\alpha$ phase. The softening that occurred following prolonged ageing was due to the heterogeneous formation of the fine nodular precipitates composed of the Ag-rich $\alpha_1$ phase and the Cu-rich $\alpha_2$ phase at the grain boundaries of the $\alpha$ phase.

Key words: Age-hardening, Gold alloy, Precipitation

INTRODUCTION

Dental casting gold alloys are essentially a ternary system of gold, copper and silver with small amounts of other elements. At least half the atoms of these alloys should be gold with noble metals to insure against corrosion, and a majority of these alloys exhibit obvious age-hardening characteristics. Due to the rise in the price of gold, alternative low-gold content alloys have been widely used for dental cast restorations. These dental casting low-gold alloys basically consist of gold, copper and silver as conventional dental casting gold alloys, although these alloys generally contain some quantity of palladium to preserve the tarnish and corrosion resistance.

The ternary Ag-Au-Cu system is characterized by a two-phase decomposition region in which the Ag-rich $\alpha_1$ phase and the Cu-rich $\alpha_2$ phase coexist, and ordering regions1,2). Therefore, the ternary Ag-Au-Cu alloys can show significant age-hardening in some composition regions with appropriate heat treatment. The hardening mechanisms of the ternary Ag-Au-Cu alloys have been reported to be due to phase transformations such as ordering, precipitation and spinodal decomposition3-9), depending on the composition of the alloy and on the ageing temperature. It was reported, however, that the hardening of commercial dental low-gold alloys was mostly caused by the AuCu I ordering10-14).

A unique dental low-gold alloy which contains some quantity of low-melting
metals to improve the castability is available. However, there has been no study of age-hardening in such an alloy. The aim of the present study was to clarify the age-hardening characteristics in a dental low-gold alloy containing some quantity of palladium and low-melting metals by means of the hardness test, X-ray diffraction (XRD) study, scanning electron microscopic (SEM) observations and electron probe microanalysis (EPMA).

**MATERIALS AND METHODS**

**Specimen alloy**
The specimen alloy used in this study was a commercial dental low-gold alloy of nominal composition with 40.0 wt% Au - 35.0 wt% Ag - 7.9 wt% Pd - 7.0 wt% Cu - 5.0 wt% In - 3.5 wt% Zn - 1.5 wt% Sn (Pontallor-4, Degussa AG, Germany).

This dental low-gold alloy is based on the Ag-Au-Cu system in its composition. In comparison with conventional dental high-gold alloys, the content of gold is reduced to 40.0% by weight. This alloy contains some quantity of palladium as a replacement for gold to preserve the tarnish and corrosion resistance, and a small quantity of low-melting metals to improve the castability. This alloy has the lower melting temperature range from 770°C to 850°C, which was manifested by the manufacturer, compared with conventional dental high-gold alloys. The lower melting temperature was suggested to be derived from the addition of low-melting metals such as indium and zinc.

**Heat treatment**
All specimens were first subjected to solution treatment at 700°C for 30 min under an argon atmosphere and then quenched into ice brine, and were subsequently aged isothermally at 350, 400 and 450°C for various periods of time in a molten salt bath and then quenched in ice brine.

**Hardness test**
Plate specimens for the hardness test were solution-treated and aged at given ageing temperatures for up to 50,000 min. Hardness measurements were made on the heat-treated specimens using a microhardness testing machine (MVK-H1, Akashi Co., Japan) with a 300 gf load and a 10 s holding time. Vickers hardness results were obtained as the average values of five measurements.

**X-ray diffraction study**
Powder specimens for the XRD study were obtained by filing the alloy and were vacuum-sealed in a silica tube, and then were subjected to the required heat treatment. The XRD studies were carried out on the heat-treated specimens using an X-ray diffractometer (D/Max-2400, Rigaku Denki Co. Ltd., Japan). The X-ray diffractometer was operated at 40 kV and 50 mA. Nickel-filtered Cu Kα radiation was used as the incident beam.
Scanning electron microscopic observation and Electron probe microanalysis
Plate specimens for the SEM observations were subjected to the required heat treatment, and then were prepared by utilizing 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. The specimens were examined at 15 kV using a scanning electron microscope (S-4200, Hitachi, Japan).

EPMA was made on the plate specimens used for the SEM observations. The specimens were examined at 15 kV using an electron probe X-ray microanalyser (EPMA-1600, Shimadzu, Japan).

RESULTS AND DISCUSSION

Age-hardening behavior
Hardness was determined as a function of time by the isothermal ageing of the solution-treated specimen at 350, 400 and 450°C. Isothermal age-hardening curves are shown in Fig. 1. The results of the isothermal ageing in the 350, 400 and 450°C temperature range showed a similar tendency in the changes. The hardness began to increase rapidly from the initial stage of ageing and reached a maximum value. Thereafter, the hardness decreased slowly by prolonged ageing. It is implied that some phase transformations occur by the isothermal ageing. As known in general diffusion process, it is obvious that the higher the ageing temperature, the shorter the time attained to the maximum hardness.

Applying an Arrhenius plot for the time to reach the hardness peak, a straight line was obtained as shown in Fig. 2. An activation energy of 26.7 kcal/mol for the hardening reaction was calculated from the slope. This value is nearly equal to 24.8
kcal/mol\textsuperscript{15)} for the migration energy of copper in silver. This suggests the migration for annihilation of excess vacancies which were introduced by quenching. It was suggested that the hardening was produced by some phase transformation by migration of copper solute atoms.

Fig. 2 Arrhenius plot of hardness.

Fig. 3 XRD patterns of the specimens solution-treated at 700°C for 30 min and aged at 350, 400 and 450°C for 10,000 min.
Parent and product phases
Fig. 3 shows the XRD patterns of the specimens solution-treated at 700°C for 30 min and aged at 350, 400 and 450°C for 10,000 min. The solution-treated specimen gives an XRD pattern of two phases (α + β). The XRD analysis revealed that the α phase had a face-centered cubic (fcc) structure with a lattice parameter of \( a_{200} = 4.021 \) Å, and the β phase had a body-centered cubic (bcc) ordered structure with \( a_{110} = 3.157 \) Å, namely a CsCl (L2₀) type structure. The superlattice reflections are not indicated in the figure because they were very weak.

By ageing at 350, 400 and 450°C, two phases (α + β) were transformed into three phases (α₁ + α₂ + β). The α₁ and α₂ phases of the specimen aged at 400°C for 10,000 min were identified as an fcc structure with \( a_{200} = 4.076 \) Å and \( a_{200} = 3.844 \) Å, respectively. The β phase of the specimen aged at 400°C for 10,000 min was identified as a bcc structure with \( a_{110} = 3.162 \) Å.

Microstructural changes and element distribution
Fig. 4 shows SEM photographs obtained from the specimens solution-treated and aged at 400°C for 5 min and 10,000 min. The SEM photograph of the solution-treated
specimen (Fig. 4(A)) represented two phases, consisting of many particles and the equiaxed structures. This result was an good agreement with that of the XRD study (Fig. 3). It is evident from the results of the XRD analysis that the black ground must be of the $\alpha$ phase with an fcc structure, and the particles must be of the $\beta$ phase with a bcc structure.

Fig. 4(B) is the SEM photograph of the specimen aged at 400°C for 5 min, at which the maximum hardness have been attained. The fine nodular precipitates were visible at the grain boundaries of the black ground. The particles were also observed as shown in Fig. 4(A). The hardness increased rapidly at the initial stage of ageing and reached a maximum value for 5 min by ageing at 400°C, as can be seen in Fig. 1. It was suggested that the increase in hardness occurred before pronounced structural changes were observed in the SEM photographs. Accordingly, some changes in the grain interior are assumed.

![Figure 5](image1.png)  
**Fig. 5** Variations in the element distribution in the solution-treated specimen by EPMA line analysis.

![Figure 6](image2.png)  
**Fig. 6** Variations in the element distribution in the specimen aged at 400°C for 10,000 min by EPMA line analysis.
Fig. 4(C) is the SEM photograph of the specimen aged at 400°C for 10,000 min. Following prolonged ageing, the grains interior of the black ground were almost covered with the fine nodular precipitates. However, the particles were also observed as shown in Fig. 4(A), and significant structural changes in the particles were not recognized in comparison with Fig. 4(A). Consequently, the fine nodular precipitates can be suggested to be composed of the $\alpha_1$ and $\alpha_2$ phases with an fcc structure from the results of the XRD analysis (Fig. 3). In addition, advancing the fine nodular precipitates into the grain interior coincided with the decrease in hardness (Fig. 1). This implies that the softening is due to the growth of the nodular precipitates, as reported in dental alloys.\textsuperscript{8,10,16–19}

Figs. 5 and 6 show variations in the element distribution in the specimens solution-treated and aged at 400°C for 10,000 min by EPMA line analysis, respectively. Particles exist as a common feature, although there are some differences between both profiles of the element distribution, the line profiles reveal that the particle corresponds to an In, Pd and Zn-rich phase. Such an element gradient must be produced by atomic diffusion during the long annealing. Judging from the lattice parameter mentioned above and the In-Pd, In-Zn and Pd-Zn phase diagrams,\textsuperscript{20} it is suggested that the particles have a CsCl-type ordered structure based on the InPd phase. The InPd phase exists as a solid state from lower temperature to 1,285°C.\textsuperscript{20} Accordingly, the particles based on the InPd phase must be stable during solution treatment at 700°C and ageing at 350, 400 and 450°C. Crystal information of the InPd phase was reported to be of a CsCl-type ordered structure with a lattice parameter of $a=3.25\text{Å}$.\textsuperscript{21} The lattice parameter ($a_{110}=3.157\text{Å}$) of the $\beta$ phase was somewhat smaller than that of the reference. It was suggested that the smaller lattice parameter of the $\beta$ phase was because the $\beta$ phase contains Zn atoms with smaller atomic size.

On the other hand, it is obvious that both matrix in the solution-treated specimen and fine nodular precipitates in the aged specimen, indicated similar element distribution, namely Ag, Au and Cu-rich tendency. Ageing at 400°C produced the following reaction from the grain boundaries;

$$a_{(fcc)} \rightarrow \alpha_1_{(fcc)} + \alpha_2_{(fcc)}$$

The two-phase decomposition agrees with the suggested Ag-Au-Cu ternary phase diagram. The relative composition of gold, copper and silver which were the main constituents in the black ground was calculated from the nominal composition to be 50.9 at% Ag - 31.8 at% Au - 17.3 at% Cu. Fig. 7 represents the suggested isothermal section of the Ag-Au-Cu ternary phase diagram at 350°C, in which the relative composition of the Ag-Au-Cu system is indicated by a solid circle. The relative composition of the Ag-Au-Cu system is located in the co-existence region of the Ag-rich $\alpha_1$ phase and the Cu-rich $\alpha_2$ phase at 350°C.

**Phase changes**

Fig. 8 shows changes in the XRD pattern during the isothermal ageing at 400°C for
the time periods indicated. As mentioned previously, two phases of the $\alpha$ phase and the $\beta$ phase based on the InPd phase were transformed into three phases of the Ag-rich $\alpha_1$ phase and the Cu-rich $\alpha_2$ phase and the $\beta$ phase. As can be seen in the isothermal age-hardening curve at 400°C (Fig. 1) and the changes of the XRD pattern during the isothermal ageing at 400°C (Fig. 8), the diffraction peaks of the $\beta$ phase

Fig. 7 Suggested isothermal section of the Ag-Au-Cu ternary phase diagram at 350°C.

Fig. 8 Changes in the XRD pattern during the isothermal ageing at 400°C.
did not exhibit characteristic changes during the age-hardening. On the other hand, some changes of the diffraction peaks of the $\alpha$ phase were detected in the early stage, which produced remarkable hardening.

During the rapid increase in hardness, the 111 diffraction peak of the Ag-rich $\alpha_1$ phase began to appear around $2\theta = 38.2^\circ$ from the initial stage of ageing, and then increased in intensity with the decrease in intensity of the 111 diffraction peak of the $\alpha$ phase. In contrast, the 200 diffraction peak of the Ag-rich $\alpha_1$ phase was superimposed with that of the $\alpha$ phase.

The appearance of the diffraction peaks of the Ag-rich $\alpha_1$ phase seems to be correlated with the nucleation of the Cu-rich $\alpha_2$ phase. However, the diffraction peaks of the Cu-rich $\alpha_2$ phase could not be detected during the hardening. The increase in hardness occurred before the pronounced structural changes were observed in the SEM photographs (Fig. 4), and before the diffraction peaks of the Cu-rich $\alpha_2$ phase were detected in the changes in the XRD pattern (Fig. 8). The above results suggests that the initial hardening is attributed to the nucleation of the Cu-rich $\alpha_2$ phase in the grain interior of the $\alpha$ phase.

Fig. 9 shows variation in the 200 diffraction angle during the isothermal ageing at 400°C. There was one step variation. In the early stage until 5 min, it clearly moves toward the lower angle side. Thereafter, it holds a constant angle. As can be seen in Fig. 1, the former corresponds to the hardening, and the latter does the softening.

Shift of the 200 diffraction peak during the hardening provides evidence for a homogeneous mechanism of the transformation. By Krawitz and Sinclair$^{22}$, such a change in the lattice parameter suggests that some precipitation in the matrix occurs. From a shift to the lower angle side, a precipitate with a higher diffraction
angle must be produced in the matrix, namely having a smaller lattice parameter. Compared to the value of the lattice parameter and this stage being due to migration of the copper solute atom as mention above, it is suggested that some Cu-rich phase was produced.

From 5 min of ageing at 400°C, at which the maximum hardness was attained, another new diffraction peaks began clearly to be detected around $2\theta = 40.7$ and 47.3. These diffraction peaks were identified as the 111 and 200 diffraction peaks of the Cu-rich $\alpha_2$ phase from the low diffraction angle, respectively. The gradual decrease in hardness occurred after showing the maximum hardness by prolonged ageing. The diffraction peaks of the Ag-rich $\alpha_1$ phase and the Cu-rich $\alpha_2$ phase gradually increased in intensity during the softening. This result is consistent with that of the SEM observations.

The 200 diffraction peak, however, did not show a shift in the angle during the softening. This suggests a heterogeneous mechanism of the transformation. Thus, it can be considered that the fine nodular precipitates composed of the Ag-rich $\alpha_1$ phase and the Cu-rich $\alpha_2$ phase at the grain boundaries of the $\alpha$ phase were formed by a heterogeneous mechanism.

REFERENCES


