

Age-hardening by miscibility limit in a multi-purpose dental gold alloy containing platinum

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Abstract

This study examined the age-hardening by miscibility limit in a multi-purpose dental gold alloy containing platinum. The hardness increased rapidly in the initial stage of the aging process, reached the maximum value, then decreased continuously with aging time. The significant hardness increase resulted from the heterogeneous precipitation of the Pt-rich β phase from the grain boundary of the Au-rich α_1 matrix due to the miscibility limit of Au-Pt system. With increasing aging time, the fine Pt-rich β precipitates covered almost the whole matrix, and by further aging, the precipitates grew coarse. The microstructural coarsening reduced the interface between the Au-rich α_1 matrix and the Pt-rich β precipitates, which released the lattice strains between the two phases, resulting in a softening effect. In the later stage of aging process, the Au-containing Pt_3In particle-like structure was transformed into the Au-depleted particle-like structure containing relatively large amounts of Cu resulting from the overlapping miscibility limit of both Au-Pt and Ag-Cu systems, which was responsible for the slow decreasing rate in hardness in the later stage of aging.

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1 Introduction

The physiology of the oral cavity and dental structures together produce a complex environment that promotes corrosion; the electrolytic corrosion between dissimilar metal restorations must be considered [1]. The application of a single alloy for all indications reduces the possibility of corrosion in the oral cavity. For this reason, a new, multi-purpose dental casting gold alloy was developed.

Conventional dental casting gold alloys of type III or IV exhibit obvious age-hardening characteristics by an appropriate heat treatment, and most of the gold alloys for ceramic-metal restorations harden during the firing of the ceramic. Several solid transformations are the probable mechanism by which the hardening process takes place. The AuCu I ordered phase with a face-centered tetragonal (fct) structure plays an important role in the hardening of conventional dental casting gold alloy which belong to type III or IV [2-7]. The ordered phases with a face-centered cubic (fcc) structure play an important role in the hardening of the gold alloy for ceramic-metal restorations [8-11].

The composition of the multi-purpose dental casting gold alloy is dissimilar in alloy composition from the dental casting gold alloy or the gold alloy for ceramic-metal restorations; there are few studies on the age-hardening mechanism of the multi-purpose dental casting gold alloy. The present study examines the mechanism of hardening and overaging in a multi-purpose dental gold alloy containing platinum. Platinum is one of the minor constituents added in dental casting gold alloy because of the high corrosion resistance and its strengthening effect in a solid solution state. In the gold alloy for ceramic-metal restorations, platinum reduces the thermal coefficient of expansion to facilitate bonding when the ceramic coating is applied to match the

Table 1: Chemical composition of the alloy

Composition	Au	Ag	Pt	Cu	In	Zn	Sn	Ir
wt%	72.1	10	9.2	4.8	3.1	0.5	0.2	0.1
at%	59.20	14.99	7.63	12.22	4.37	1.24	0.27	0.08

surrounding natural teeth. Platinum has a miscibility limit with the major constituent, gold, in the solid state [12], which may or may not affect the age-hardening mechanism depending on the alloy composition. The purpose of the present study is to elucidate the age-hardening mechanism of a multi-purpose dental gold alloy containing platinum, by examining the hardening behavior, phase transformation, changes in microstructure, and element distribution during aging.

2 Experimental details

The alloy used in the present study was a multi-purpose Au-Ag-Pt-Cu-In alloy (Aurium bio 422, Aurium research, U.S.A.). The chemical composition of the alloy is listed in Table 1. The initial shape of the specimen was plate-like with dimensions of 9 mm × 9.5 mm × 1 mm, and was procured in a rolled and annealed state.

Before hardness testing, the specimens were solution-treated at 850°C for 10 min under an argon atmosphere, and then rapidly quenched into ice brine to prevent thermal changes on cooling. Specimens were subsequently aged isochronally for 10 and 20 min in the temperature range of 200°C to 550°C, and were isothermally aged at 350°C and 400°C for various periods of time. All aging was performed in a molten salt bath, followed by quenching in ice brine. Hardness measurements were made using a Vickers micro-hardness tester (MVK-HI, Akashi Co., Japan) with a load of 300 gf and a dwell time of 10 s. Vickers hardness results were recorded as the average values of 5 measurements.

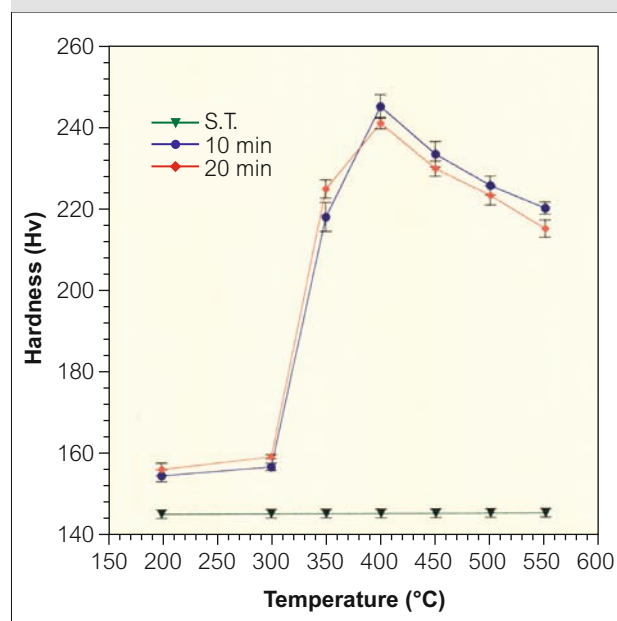
For the X-ray diffraction (XRD) studies, powder specimens that passed through a 300-mesh screen were obtained by filing the plate-like specimens. After vacuum-sealing in a silica tube and solution-treated at 850°C for 10 min, they were isothermally aged at 350°C for various period of time in a molten salt bath, and then quenched into ice brine. The X-ray diffraction profiles were recorded by an X-ray diffractometer (D/Max-2400, Rigaku Denki

Co. Ltd., Japan). The X-ray diffractometer was operated at 30 kV and 40 mA, using Ni-filtered Cu K α radiation.

For the filed emission scanning electron microscopic (FE-SEM) observations, the plate-like specimens were subjected to the required heat treatment, and then prepared by utilizing standard metallographic techniques. A freshly prepared aqueous solution of 10% potassium cyanide and 10% ammonium persulfate was used for the final etching of the specimens. The specimens were examined at 15 kV using a filed emission scanning electron microscope (JSM-6700F, JEOL, Japan).

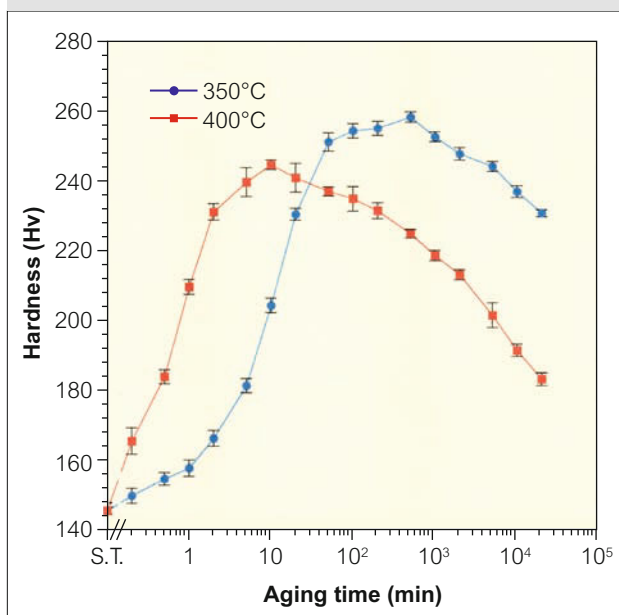
For the energy dispersive spectrometer (EDS) analysis, the specimens were prepared in the same manner as was used for the FE-SEM observations. EDS analysis was performed using a field emission

Figure 1



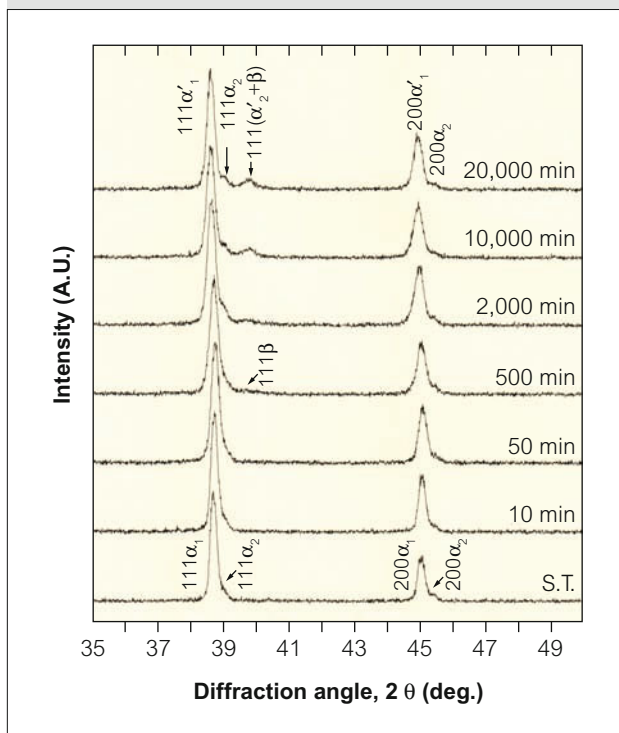
The isochronal age-hardening curves of the specimen alloy solution-treated at 850°C for 10 min, and then aged in the temperature range of 200°C to 550°C for 10 and 20 min

Figure 2



The isothermal age-hardening curves of the alloy solution-treated at 850°C for 10 min and then aged for various times at 350°C and 400°C

Figure 3



The variations of the XRD pattern during 350°C isothermal aging

scanning electron microscope (JSM-6700F, JEOL, Japan) equipped with an energy dispersive X-ray spectrometer (INCA x-sight, Oxford Instruments Ltd., UK).

3 Results and discussion

3.1 Hardness change

To determine an appropriate aging temperature, the specimens were isochronally aged in the temperature range of 200°C to 550°C. Fig. 1 shows the isochronal age-hardening curves of the specimen alloy solution-treated at 850°C for 10 min, and then aged in the temperature range of 200°C to 550°C for 10 and 20 min. The alloy exhibited an apparent age-hardenability near 400°C. Thus, the age-hardening behavior with aging time was observed at 350°C and 400°C.

Fig. 2 shows the isothermal age-hardening curves of the alloy solution-treated at 850°C for 10 min and then aged for various times at 350°C and 400°C. The isothermal age-hardening curves at 350°C and 400°C displayed a similar tendency, but the aging rate was more rapid at 400°C than at 350°C due to the faster atomic diffusion at higher aging temperature [13-16]. The hardness of the solution-treated specimen began to increase and reached a maximum value with increasing aging time, and then the hardness decreased constantly. Considering the overall age-hardening curve, the age-hardenability and the age-hardening behavior were similar at 350°C and 400°C; this suggested that the same age-hardening mechanism occurred at both temperatures.

3.2 XRD study

Variations of XRD pattern during isothermal aging were examined to clarify a relation of the phase transformation and the hardness change during aging process. Fig. 3 shows the variations in the XRD pattern during 350°C isothermal aging. The XRD pattern of the solution-treated specimen demonstrated two phases, α_1 and α_2 . The α_1 phase was the Au-rich phase having a face-centered cubic (fcc) structure with a lattice parameter of $a_{200}=0.4026$ nm. The α_2 phase was an ordered fcc phase based on Pt_3In with a lattice parameter of $a_{200}=0.3992$ nm [17], as it will be shown in section 3.4.

By aging the solution-treated specimen at 350°C for 20,000 min, the α_1 phase was transformed into the α'_1 phase with $a_{200}=0.4028$ nm by precipitating

the β phase. The α_2 phase was in the process of transformation into the α_2' phase, showing a peak overlap with the β phase at the aging time of 20,000 min, this will be described further later. Upon analysis it was determined that the β phase was the Pt-rich fcc phase with the lattice parameter of $a_{111}=0.3926$ nm at the aging time of 500 min [18].

Changes in the XRD patterns during the isothermal aging at 350°C were examined with respect to the isothermal age hardening curve at 350°C (Fig. 2). Until the aging time of 500 min when the maximum hardness value was obtained, the β phase of very weak peak intensity formed, and the α_1 peaks were broadened. The α_2 peaks did not show apparent changes in position and intensity until reaching the 500 min time point. The broad peaks of the α_1 phase indicated that the lattice strains that cause the hardness increase formed in the α_1 matrix by precipitating the β phase [13,19,20].

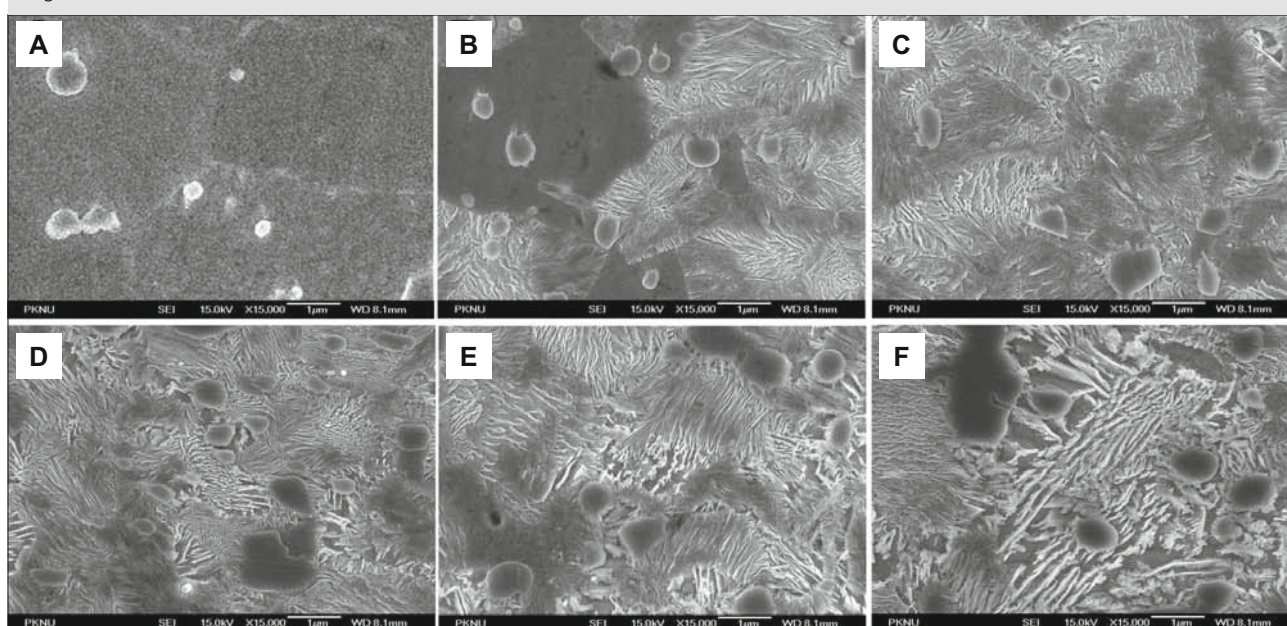
During the period of hardness decrease after 500 min, the peak intensity of the α_2 phase decreased, and that of the β phase increased. In addition, α_1 peaks shifted a little toward the lower diffraction angle. Considering the XRD peak position, it can be supposed that the Pt_3In α_2 phase was in the process of transformation into the Pt-rich β phase by precipitating In or into the Pt_3In α_2' phase with a smaller lattice parameter than the α_2 phase by

absorbing elements of relatively small atomic size from the matrix. This will be clarified in section 3.4. The broad peaks of the α_1 phase remained broad during the transformation of the α_2 phase, indicating large amounts of lattice strains in the matrix. This corresponded to the fact that the hardness kept a relatively high value for a long time in the later stage of aging process.

3.3 Microstructural changes

FE-SEM observations were performed to clarify the microstructural changes related to the hardness changes. Fig. 4 demonstrates the FE-SEM photographs of 15,000 magnification for the specimens that were solution-treated at 850°C for 10 min (A) and aged at 350°C for 50 min (B), 500 min (C), 2000 min (D), 10,000 min (E) and 20,000 min (F). In the solution-treated specimen (A), matrix and particle-like structure were observed. From the XRD peaks intensity, it was clear that the matrix was the α_1 phase of higher peaks intensity, and the particle-like structure was the α_2 phase. By aging the specimen at 350°C for 50 min (B) when the hardness increased up to 96% of the maximum value, the fine precipitates grew and covered more than half of the matrix from the grain boundaries toward the grain interior. By further aging for 500 min (C) when the maximum hardness value was obtained, the fine precipitates covered almost the whole matrix. The particle-like structure of various sizes did not show

Figure 4



The FE-SEM photographs of 15,000 magnification for the specimens solution-treated at 850°C for 10 min (A) and aged at 350°C for 50 min (B), 500 min (C), 2000 min (D), 10,000 min (E) and 20,000 min (F)

apparent changes. Considering the corresponding XRD pattern which showed that the α_1 peak was broadened as the weak β peak appeared, it was judged possible that the significant hardness increase resulted from the heterogeneous precipitation of the Pt-rich β phase from the grain boundary of the Au-rich α_1 matrix due to the miscibility limit of the Au-Pt system in solid state.

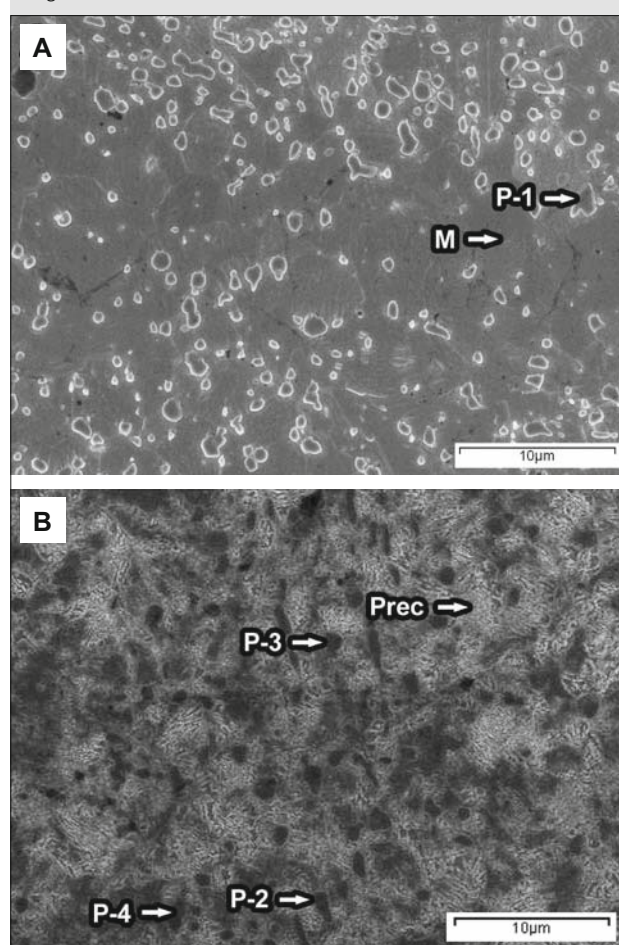
By further aging the specimen for 2000 min (D), 10,000 min (E), 20,000 min (F) when the hardness decreased by 4%, 8% and 11% of the maximum value, respectively, the fine precipitates grew coarse with aging time. The microstructural coarsening reduced the interface between the Au-rich α_1 matrix and the Pt-rich β precipitates, which released the lattice strains between the two phases, resulting in a softening effect [7,11]. Even with a significant decrease in the α_2 peak intensity during the period of hardness decrease, the α_2 particle-like structure did not show apparent microstructural changes. Thus, it was supposed that the α_2 particle-like structure has undergone severe elemental distributional changes without microstructural changes. To clarify this issue, the EDS analysis was done.

3.4 The changes of element distribution

Fig. 5 shows the FE-SEM photographs for the specimens solution-treated at 850°C for 10 min (A) and aged at 350°C for 20,000 min (B). The element distribution in the matrix (M), particle-like structure (P) and precipitate (Prec) marked by an arrow were analyzed; the results are displayed in Table 2. In the matrix (M) of Fig. 5-A, an increase in Au, Ag and a decrease in Pt, In was observed compared to the base composition of Table 1. In the particle-like structure (P-1) of Fig. 5-A, large amounts of Pt and In were observed compared to the base composition. The Pt content in the particle-like structure was more than twice that of the In content and the Au

content was about 20 at% in the solution-treated state. This explained that the matrix was composed of the Au-rich α_1 phase containing Ag and Cu, and the particle-like structure was composed of the Pt_3In phase containing Au.

Figure 5



FE-SEM photographs for the specimens solution-treated at 850°C for 10 min (A) and aged at 350°C for 20,000 min (B)

Table 2: EDS analysis at the regions marked in Fig. 5

Region (at%)	Au	Ag	Pt	Cu	In	Zn	Sn
M	62.88	16.26	3.25	12.41	2.84	2.04	0.32
P-1	20.23	0	54.67	0	25.1	0	0
P-2	19.03	2.45	48.77	5.73	18.17	2.13	3.74
P-3	7.65	2.16	45.79	18.62	18.3	4.6	2.89
P-4	8.54	0.72	43.18	22.88	17.92	4.18	2.59
Prec	57.23	12.24	7.62	14.91	4.26	1.52	2.22

In the particle-like structure of the overaged specimen (Fig. 5-B), the P-2 region showed a similar elemental distribution with the P-1 region of the solution-treated specimen (Fig. 5-A). On the other hand, the P-3 and P-4 regions demonstrated an apparent increase in Cu and a decrease in Au, even though the Pt and In contents had not apparently diverged from those in the P-2 region. Zn and Sn which have low melting temperature were also included in the Pt-rich regions of P(2-4). Considering the changes in the element distribution, the severe XRD pattern changes of the α_2 phase in Fig. 3 were mainly caused by the atomic diffusion of Cu and Au. Au and Pt have a miscibility limit for each other in the solid state [21]. In the solution-treated specimen at 850°C, the Pt₃In particle-like structure contained Au by 20 at%, but by aging the specimen at lower temperatures, such as 350°C, excess amounts of Au diffused from the Pt-concentrated particle-like structure to the surrounding Au-rich matrix. In the same manner, Cu which has the miscibility limit for Ag in solid state, could not dissolve in the Ag-concentrated Au-rich matrix, and thus excess amounts of Cu diffused to the particle-like structure from the matrix [12]. Based on the evidence described above, it became clear that the Au-containing Pt₃In particle-like structure was in the process of transformation into the Au-depleted particle-like structure containing relatively large amounts of Cu due to the overlapped miscibility limit of both Au-Pt and Ag-Cu systems in solid state. Due to such elemental distributional changes in the matrix and particle-like structure, the hardness decreasing rate became relatively slow even with the progress of coarsening of the Pt-rich β precipitates. In the precipitates (Prec) of the overaged specimen (Fig. 5-B), high contents of Au and Ag were detected, and the content of Pt, Cu, In and Sn increased compared to that in the matrix (M). Considering that the contents of Au and Ag were inevitably reflected from the surrounding Au-rich matrix containing Ag due to the sampling spot size, the precipitates appeared to be the Pt-rich β phase containing In, Cu and Sn at the aging time of 20,000 min.

Conclusions

Age-hardening by miscibility limit in a multi-purpose dental gold alloy containing platinum was examined, and the following results were obtained.

- 1 The hardness increased rapidly in the initial stage of the aging process, reaching the maximum value, and decreased continuously with aging time.
- 2 The hardness increase was caused by the precipitation of the Pt-rich β phase from the grain boundary of the Au-rich α_1 matrix due to the miscibility limit of Au-Pt system in solid state.
- 3 The microstructural coarsening reduced the interface between the Au-rich α_1 matrix and the Pt-rich β precipitates, which released the lattice strains between the two phases, resulting in a softening effect.
- 4 The Au-containing Pt₃In particle-like structure was transformed into the Au-depleted particle-like structure containing relatively large amounts of Cu due to the overlapped miscibility limit of both Au-Pt and Ag-Cu systems, which was responsible for the slow decreasing rate in hardness in the later stage of aging.

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