Age-hardening by grain interior and grain boundary precipitation in an Au-Ag-Pt-Zn-In alloy for multipurpose dental use

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Abstract

The complex precipitation mechanisms related to the age-hardening of Cu-free Au-Ag-Pt-Zn-In alloy for multipurpose dental use was studied by means of hardness test, X-ray diffraction (XRD) studies, field emission scanning electron microscopic (FE-SEM) observations, energy dispersive spectrometer (EDS) analysis, and electron probe microanalysis (EPMA). The early diffusion and then clustering of the In-concentrated phase in the grain interior, together with the early diffusion and then ordering of the PtZn phase in the grain boundary, introduced the internal strains in the Au-Ag-rich α_1 matrix, resulting in the hardening process. As the Au-Ag-rich α_1' and PtZn β lamellar-forming grain boundary reaction progressed, the phase boundaries between the solute-depleted face-centered cubic (FCC) α_1' matrix and the face-centered tetragonal (FCT) PtZn β precipitate reduced, resulting in softening. In the particle-like structures composed of the major Pt-Au-rich α_2 phase and the minor Pt-Zn-rich α_3 phase, the separation of In and Zn progressed producing the In-increased Pt-Au-rich α_2' phase and the

Zn-increased PtZn α_3' phase with aging time without restraining the softening. The miscibility limit by complex systems of Au-Pt, Ag-Pt, Au-In and In-Zn resulted in the phase transformation and related microstructural changes.

1 Introduction

The majority of dental gold alloy is composed of an Au-Ag-Cu system with additives. The ternary Au-Ag-Cu system is characterized by decomposition regions into the Ag-rich and Cu-rich regions and an AuCu ordering region. This chemical characterization is the result of Ag and Cu having limited miscibility, while Au is completely soluble with both Ag and Cu at any atomic ratio [1]. Thus, the hardening mechanism is usually attributed by dual mechanisms of phase separation into Ag-rich and Cu-rich, and then ordering which forms the AuCu I ordered phase with a face-centered tetragonal (FCT) structure in the Cu-rich regions [2-6]. These types of dental gold alloys, the Au-Ag-Cu system cannot use as the basis of ceramic-metal restorations due to the relatively low melting temperature and a high thermal coefficient of expansion. In order to mitigate these problems, a relatively large amount of Pt was added to the basic dental gold alloy system, which allows the new dental gold alloy for multiple indications.

The multipurpose dental gold alloy composed of Cu-free Au-Ag-Pt-Zn-In was examined in this study. The major components, Au and Ag, have a miscibility limit with Pt in solid state, which can be seen in the binary phase diagrams of Au-Pt and Ag-Pt systems [1]. The minor ingredients, In and Zn, represent a simple eutectic in the assessed In-Zn binary phase diagram [1]. Thus, complex precipitation mechanisms were expected based on the present alloy composite. The hardening mechanism of the gold alloy for ceramic-metal restoration is known

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to be attributed to the ordered phases with a face-centered cubic (FCC) structure [7-10], and cannot be applied to gold alloy for multipurpose dental use, as the age-hardening mechanism and related phase transformation become different with a slight compositional change. The hardening mechanism of the gold alloy for multipurpose dental use has been studied rarely and, is not clear. The aim of the present study is to examine the complex precipitation mechanisms which are related to age-hardening in a Cu-free Au-Ag-Pt-Zn-In alloy for dental multipurpose, by characterizing the hardness changes and related phase transformation, microstructural, and element distributional changes during the aging process.

2 Experimental details

The alloy used in the present study was a multipurpose Au-Ag-Pt-Zn-In alloy (Aurium 55, 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 9mm × 9.5mm × 1mm, and was procured in a rolled and annealed state.

Table 1: Chemical composition of the alloy

Composition	Au	Ag	Pt	Zn	In	Pd	Rh (+Ta+Ir)
wt%	55	23	11.7	3	3.5	3	0.8
at%	42.0	32.1	9.0	6.9	4.6	4.2	1.2

Prior to hardness testing, the specimens were solution-treated at 850°C for 15 min under an argon atmosphere, and then rapidly quenched into ice brine to preclude thermal changes on cooling. Specimens were subsequently aged isochronally for 10 and 20 min in a temperature range of 250°C to 600°C, and were isothermally aged at 500°C for various periods of time. All aging was done in a molten salt bath, followed by quenching into 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 value of 5 measurements.

For the X-ray diffraction (XRD) studies, powder specimens which passed through a 300-mesh screen were obtained by filing the plate-like specimens. After being vacuum-sealed in a silica tube and solution-

treated at 850°C for 15 min, they were isothermally aged at 500°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 (XPRT-PRO, Philips, Netherlands). The X-ray diffractometer was operated at 30 kV and 40 mA, using Ni-filtered Cu K α radiation and installed at Pusan National University.

For the field emission scanning electron microscopic (FE-SEM) observations, the plate-like specimens were subjected to the required heat treatment, and then they were prepared by utilizing standard metallographic techniques for FE-SEM examinations to observe the microstructural changes in the specimen alloy during the aging process. A freshly prepared aqueous solution composed of 10% potassium cyanide and 10% ammonium persulfate was utilized for the final etching of the samples. The specimens were examined at 20 kV using a field emission scanning electron microscope (JSM-6700F, JEOL, Japan) which was installed at Pukyong National University.

For the energy dispersive spectrometer (EDS) analysis and electron probe microanalysis (EPMA), the specimens were prepared as described above for the FE-SEM examinations. An energy dispersive X-Ray spectrometer (INCA x-sight, Oxford Instruments Ltd., UK) of an FE-SEM (JSM-6700F, JEOL, Japan) was used at 15 kV for the EDS analysis and installed at Pukyong National University. And an electron probe X-ray microanalyser (EPMA-1600, Shimadzu, Japan) was used at 15 kV for EPMA and installed at Pukyong National University.

3 Results and discussion

3.1 Age-hardening behaviour

To determine an appropriate aging temperature, the specimens were isochronally aged in the temperature range of 250°C to 600°C. Fig. 1 shows the isochronal age-hardening curves of the specimen alloy solution-treated at 850°C for 15 min, and then aged in the temperature range of 250°C to 600°C for 10 and 20 min. The alloy exhibited an apparent age-hardenability at 500°C. Thus, the age-hardening behaviour with aging time was observed at 500°C.

Fig. 2 shows the isothermal age-hardening curve of the alloy solution-treated at 850°C for 15 min and then aged for various periods of times at 500°C. The hardness of the solution-treated specimen increased

Figure 1

Isochronal age-hardening curves of the specimen alloy aged in the temperature range of 250°C to 600°C for 10 min and 20 min

Figure 2

Isothermal age-hardening curve of the specimen alloy aged at 500°C

rapidly and reached a maximum value at the aging time of 50 min. Then the hardness decreased drastically, but near the aging time of 1,000 min, the decreasing rate of hardness slowed. Finally, the hardness stopped decreasing at the aging time of 10,000 min.

3.2 Phase transformation

Variations in the XRD pattern during isothermal aging were examined during isothermal aging at 500°C to clarify a relationship between the phase transformation and the hardness change during the aging process, which is demonstrated in Fig. 3. The XRD pattern of the solution-treated specimen showed 3 phases, α_1 , α_2 and α_3 . The major α_1 phase was Au-Ag-rich phase having a face-centered cubic (FCC) structure with a lattice parameter of $a_{200}=0.4064$ nm. The α_2 phase was Pt-Au-rich phase having an FCC structure with a lattice parameter of $a_{200}=0.3992$ nm. The minor α_3 phase was Pt-Zn-rich phase having an FCC structure with a lattice parameter of $a_{111}=0.3841$ nm.

By aging the solution-treated specimen at 500°C for 20,000 min, the Au-Ag-rich α_1 phase was transformed into the Au-Ag-rich α_1' phase with an increased lattice parameter, $a_{200}=0.4082$ nm by precipitating the PtZn β phase. The α_2 and α_3 phases were transformed

Figure 3

Variations of the XRD patterns during the isothermal aging at 500°C with aging time

into the Pt-Au-In-rich α_2' phase with an increased lattice parameter of $a_{111}=0.4034$ nm and the PtZn α_3' phase with lattice parameters of $a_{110}=0.4076$ nm and $c_{002}=0.3436$ nm, respectively [11]. Both the β and α_3' phases were the same PtZn phase of AuCu I-type, but were named differently as they had originated from different phases and formed in different regions, as will be seen in the EDS analysis.

Changes in the XRD patterns during the isothermal aging at 500°C were examined with respect to the isothermal age hardening curve at 500°C (Fig. 2). At the aging time of 10 min when the hardness increased up to approximately 93% of its maximum value, the α_1 peaks shifted a little toward lower diffraction angle side, and very weak 111 β peak appeared in the higher diffraction angle side of the 111 α_3 peak. Until the aging time of 50 min when the hardness increased up to the maximum value, the 200 α_2 peak became significantly broad. Therefore, the hardness increase during the early stages of the aging process was mainly related to the phase transformation of the α_1 phase and secondarily to the α_2 phase. By further aging until 1000 min when the decreasing rate in hardness slowed, the α_2 phase transformation was apparent.

Further aging to 10,000 min when the hardness had decreased significantly from its maximum value, the transformation of the 111 α_2 peak into the 111 α_2' peak almost finished, and concurrently the 111 peak intensity of the α_3 phase decreased as that of the α_3' phase increased. This resulted from the separation of In and Zn with aging time, as will be discussed in the EDS results. From the above, in the later stage of aging process, the phase transformation of α_2 into α_2' and α_3 into α_3' progressed, and which slowed the decreasing rate of hardness for a while. The phase transformation must have produced lattice strains resulting in hardening, as it was in various dental alloys [12-15]. However, it did not stop the softening process. Therefore, it was thought that some microstructural changes resulting in softening occurred during the later phase transformation.

3.3 Microstructural changes

FE-SEM observations were performed to clarify the microstructural changes that occurred during the hardness changes. Fig. 4 is showing the FE-SEM micrographs of 2,000X, 30,000X magnifications for the specimens solution-treated at 850°C for 15 min (A) and aged at 500°C for 50 min (B), 200 min (C), 10,000 min (D) and 20,000 min (E). In the FE-SEM micrograph of the solution-treated specimen (A),

matrix and particle-like structures were observed. From the alloy composition and the XRD peaks intensity, the matrix was the α_1 phase being Au-Ag-rich, and the particle-like structures were the α_2 phase being Pt-Au-rich and the α_3 phase being Pt-Zn-rich, as will be observed in the EDS results.

FE-SEM micrographs at magnifications of 2,000X (1) and 30,000X (2) for the specimen solution-treated at 850°C for 15 min (A), and aged at 500°C for 50 min (B), 200 min (C), 10,000 min (D) and 20,000 min (E)

By aging the specimen at 500°C for 50 min (B) when the maximum hardness value was obtained, fine lamellar structures formed in limited areas of the grain boundary. The appearance of lamellar structure stopped the further increase in hardness. In the corresponding XRD pattern, the PtZn β peak began to appear as the main α_1 peak shifted toward a lower diffraction angle. Thus, it was thought that the formation of lamellar structure resulted from the precipitation of the PtZn β phase from the α_1 matrix. By aging the specimen at 500°C for 200 min (C) when the hardness decreased to 87% of the maximum value, the grain boundary lamellar structure grew further into the grain interior, and the inter-lamellar spacing became broad. And fine, dot-like precipitates covered the grain interior except the particle-like structure, which was revealed to be the In-concentrated phase that diffused from the α_1 phase, as will be discussed in the EDS results. It is thought that the microstructural changes occurred by the grain interior precipitation of the In-concentrated phase and the lamellar-forming grain boundary reaction by the PtZn phase.

By further aging the specimen for 10,000 min (D) when hardness had decreased to 65% of the maximum value, the volume fraction of the lamellar structure did not further increase. However, the inter-lamellar spacing broadened compared to the specimen that had been aged for 50 min. The transformation of the α_2 and α_3 phases did not cause apparent microstructural changes in the particle-like structure. The further coarsening of the grain boundary lamellar structure did not occur by aging the specimen for 20,000 min (E), a point at which there was no further reduction in hardness.

From the above, it can be said that both the volume fraction of lamellar structure and the inter-lamellar spacing were proportional to the decreasing rate in hardness. It was thought that the early diffusion and then clustering of the In-concentrated phase in the grain interior together with the early diffusion and then ordering of the PtZn phase in the grain boundary introduced the internal strains in the matrix. But, as the microstructural coarsening, that is, mainly lamellar-forming grain boundary reaction progressed, the phase boundaries between the FCC matrix and the FCT PtZn precipitate reduced, and thus the internal strains released, resulting in softening [6,16,17].

3.4 Element distribution

To identify the changes in element distribution produced by the aging process, the distribution of Au, Ag, Pt, Zn, In, Pd was investigated by EDS analysis and EPMA. Fig. 5 shows the FE-SEM micrographs for the specimens solution-treated at 850°C for 15 min (A) and aged at 500°C for 20,000 min (B). The element distribution in the matrix (M), particle-like structure (P) and lamellar structure (L) marked by an arrow was analyzed; the results are shown in Table 2(1,2), respectively. In the matrix (M)

Table 2.1: EDS analysis at the regions marked in Fig. 5-A for the specimen solution-treated at 850°C for 15 min

Region (at%)	Au	Ag	Pt	Zn	In	Pd
M (α_1)	51.4	36.7	1.2	3.7	3.3	3.7
P1 (α_2)	27.5	4.6	29.7	11.2	14.7	12.3
P2 (α_2)	25.8	4.6	29.5	15.2	14.8	10.1

Figure 5

FE-SEM micrographs for the specimens solution-treated at 850°C for 15 min (a) and aged at 500°C for 20,000 min (b)

Table 2.2: EDS analysis at the regions marked in Fig. 5-B for the specimen aged at 500°C for 20,000 min

Region (at%)	Au	Ag	Pt	Zn	In	Pd
M1 (α_1')	52.7	37.7	0.4	0.8	5.1	3.3
M2 (α_1')	51.7	36.1	1.6	0	6.0	4.6
P1 (α_2')	27.6	3.5	29.0	3.3	21.8	14.8
P2 (α_2')	27.2	6.2	28.7	2.8	21.0	14.1
P3 (α_3)	17.3	4.3	32.4	27.3	10.4	8.3
L1 (α_1')	49.3	37.6	2.1	4.0	3.1	3.9
L2 (β)	24.8	7.7	25.3	20.3	9.7	12.2

of Fig. 5-A and Table 2-1, an increase in Au and Ag, and a decrease in Pt was detected compared to the base composition of Table 1. In the small and large particle-like structures (P) of Fig. 5-A, the content of Au and Ag decreased, and that of Pt, Zn, In, Pd increased apparently. The amount of In and Zn in (P) regions was almost equal. From the above, it was clear that the Au-Ag-rich α_1 phase composed the matrix and the α_2 phase being Pt-Au-rich composed the particle-like structures. The minor α_3 phase being Pt-Zn-rich was not detected due to the limited distribution.

In the over aged specimen (Fig. 5-B, Table 2.2), the matrix was Pt-, Zn-depleted α_1' phase, in which the content of In increased slightly compared to that in the solution-treated specimen (M1,2). In the FE-SEM micrograph, the matrix that was not replaced by the lamellar structure was covered by fine, dot-like structures. Thus, the increase of In indicated that the In-concentrated phase precipitated out from the solute-saturated grain-interior to form the fine, dot-like structures covering the matrix, even though the amount was not enough to be detected in the XRD peaks. Such a result can be expected from the Au-In binary phase diagram showing the decreasing miscibility of In, in the Au-rich phase with decreasing aging temperature [1].

In the lamellar structure, an Au-Ag-rich layer (L1) and a Pt-Zn-rich layer (L2) were observed. It is possible that the elemental content detected in each layer of the lamellar structure contained elements of the neighboring layer to an extent, due to its fine nature. However, by considering the EDS results together with the obtained lattice parameter and the alloy composition, the lamellar structure was composed of the alternating Au-Ag-rich α_1' and PtZn β layers.

In dental Au-Ag-Cu alloys forming lamellar structure, a distributional inequality of Au is unusual in each layer of lamellar structure; because Ag and Cu have limited miscibility, while Au is completely soluble with both Ag and Cu [1,18,19]. In the present study with Au-Ag-Pt alloy, the content of Au, together with Ag, was unequal in each layer of the lamellar structure, which was resulted from decreasing miscibility with decreasing aging temperature in Au-Pt and Ag-Pt systems [1,20].

The composition of the particle-like structures changed apparently at 20,000 min. In the P(1,2) regions of Fig. 5-B, the content of In increased and that of Zn decreased apparently compared to that in the α_2 phase at P regions of Fig. 5-A. By considering the XRD results together, it can be concluded that the α_2 phase being Pt-Au-rich containing equal amounts of Zn and In was transformed into the Pt-Au-rich α_2' phase of In-increased and Zn-depleted. In the P3 region of Fig. 5-B, the Pt-Zn-rich α_3 phase was detected, in which the contents of Zn were about three times of In. The minor α_3' phase was undetectable due to the limited distribution.

The EPMA analysis showed the same results as the EDS analysis. Fig. 6 shows the EPMA results of the specimen solution-treated at 850°C for 15 min (A) and aged at 500°C for 20,000 min (B). It is clear in Fig. 6 (A) that the distribution of Pt, Pd and In was contrast to that of Ag and Au. In the particle-like structures, the Zn-rich regions were almost overlapped with the Pt-, Pd- and In-rich regions. However, after aging a specimen at 500°C for 20,000 min (B), the overlapped regions of Zn with Pt-, Pd- and In-rich regions had decreased apparently in the particle-like structures.

The XRD results showed that the α_2 peak shifted toward a lower diffraction angle, as the α_3 peak shifted toward a higher diffraction angle. Considering the above EDS results together with the XRD pattern changes, Zn that has a relatively small atomic size diffused out from the α_2 phase to the α_3 phase, and In that has a relatively large atomic size diffused out from the α_3 phase to the α_2 phase in the particle-like structures [21]. The In-Zn binary phase diagram shows the eutectic, which indicated that repulsive force works between In and Zn [1]. From the above, it can be concluded that the Pt-rich particle-like structures were composed of the major Pt-Au-rich α_2 regions containing equal amounts of Zn and In and the minor Pt-Zn-rich α_3 regions in which the contents of Zn were about three times of In, and where the

Figure 6

EPMA results of the specimen solution-treated at 850°C for 15 min (a) and aged at 500°C for 20,000 min (b)

separation of In and Zn progressed with aging time without apparent microstructural changes. In the study with an Au-Ag-Cu-Pt-In alloy, the Au-containing Pt₃In particle-like structure was transformed into the Au-depleted particle-like structure containing relatively large amounts of Cu that was diffused from the Au-Ag-rich matrix, and which resulted from the overlapped miscibility limit of both Au-Pt and Ag-Cu systems [20]. However, in the present study with an Au-Ag-Pt-Zn-In alloy, such an Au-depletion in the Pt-rich particle-like structure was not observed after transformation, as can be seen in Table 2(1,2). From such a fact, it was supposed that the separation of In and Zn occurred preferentially, suppressing the separation of Au out of the Pt-rich particle-like structure due to the large degree of immiscibility in the In-Zn system.

Conclusions

This study examined the complex precipitation mechanisms which are related to age-hardening in a dental Au-Ag-Pt-Zn-In alloy for multipurpose dental use, and the conclusions are as follows.

1. The optimum heat treatment for the Au-Ag-Pt-Zn-In alloy was achieved by aging at 500°C for 50 min after solution-treatment at 850°C for 15 min.
2. The Au-Ag-rich α_1 matrix was transformed into the Au-Ag-rich α_1' matrix with aging time by precipitating the In-concentrated phase in the grain interior and the PtZn β phase in the grain boundary, resulting in the hardening process.
3. The softening occurred as the Au-Ag-rich α_1' and PtZn β lamellar-forming grain boundary reaction progressed. Both the volume fraction of lamellar structure and the inter-lamellar spacing were proportional to the decreasing rate in hardness.
4. In the particle-like structures composed of the major Pt-Au-rich α_2 phase and the minor Pt-Zn-rich α_3 phase, the separation of In and Zn progressed producing the In-increased Pt-Au-rich α_2' phase and the Zn-increased PtZn α_3' phase with aging time without restraining the softening.
5. The miscibility limit by complex systems of Au-Pt, Ag-Pt, Au-In and In-Zn resulted in the phase transformation and related microstructural changes.

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