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시판 치과용 Au-Ag-Cu-Pd 합금의 등온시효경화거동

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= Abstract =

Isothermal Age-hardening Behavior in the Commercial Dental Au-Ag-Cu-Pd Alloy

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The relationship between the isothermal age-hardening behavior and the phase transformation in the commercial dental Au-Ag-Cu-Pd alloy was investigated.

Age-hardening was mostly attributed to the lattice distortions of the supersaturated α phase resulting from the transformation to the metastable phases, which were more distinct at lower aging temperature. The lattice distortions resulting from the transformation of the metastable phases to the equilibrium phases also made a contribution to the age-hardening.

Key words : Age-hardening, Metastable phase, Equilibrium phase, Lattice distortion

INTRODUCTION

Conventional dental casting gold alloys are essentially ternary alloys of gold, silver and copper with small amounts of other elements. Because of the increased cost of noble metals, especially that of gold, many alternative dental low carat gold alloys have been introduced commercially and have been widely used for dental cast restorations. These alloys contain palladium to preserve the tarnish and corrosion resistance. It has been well known that the ternary Au-Ag-Cu alloys show significant age-hardening in a certain composition region by appropriate heat treatment and that the addition of palladium to ternary Au-Ag-Cu alloys gives rise to conspicuous age-hardening.

It was observed in an experimental Au-35.4at.% Cu-17.8at.% Ag-9.7at.% Pd alloy that the age-hardening was caused by the formation of the AuCu I type tetragonal superlattice nuclei in the disordered matrix[1]. It was also reported that the aging process in the 16 and 14 carat gold commercial dental alloys containing palladium consisted of two stages[2,3]. The initial age-hardening was due to the introduction of coherency strain at the interface between the matrix and the metastable AuCu I' ordered phase which was first reported by Hisatsune et al.[4,5] Furthermore, the drastic decrease in hardness by prolonged aging was brought about due to the loss of coherency at the interface of the lamellar structure which was formed at grain boundaries. Kim and Choi[6] reported that the overaging with softening in the 13 carat gold commercial dental Au-Ag-Cu-Pd alloy was due to the broad precipitates formation of the lamellar structure which was composed of the AuCu I ordered fct phase containing Pd and the Ag-rich α_1 solid solution fcc phase containing Au.

The age-hardening mechanism varies greatly depending on the combinations of constituents and the compositions of the constituents. In addition, the age-hardening behavior of the alloy which has the same composition varies with the aging temperatures.

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Table 1. Nominal composition of specimen alloy

	Au	Ag	Cu	Pd	Pt	Zn	Ir
wt.%	58.0	23.3	12.0	5.5	≤2	≤2	≤2
at.%	39.2	28.8	25.1	6.9			

Yasuda et al.[2] and Udoh et al.[3] reported that the age-hardening was attributed to the single process of the AuCu I' ordering independent of the aging temperatures, and Kim and Choi[6] did not elucidate the age-hardening mechanism. Therefore, the present study attempted to elucidate the relationship between the isothermal age-hardening behavior and the phase transformation of the dental low-carat Au-Ag-Cu-Pd alloy at various temperatures.

MATERIALS and METHODS

The specimen alloy used in this study is a commercial dental low carat gold alloy(Stabilor G Alloy, Degussa, Germany). The nominal composition of the alloy is given in Table 1.

All specimens were solution-treated at 750℃ for 30min to obtain a supersaturated single phase and then quenched into ice brine, and were isothermally aged at 350~450℃ for the various ranges of time in a molten salt bath and then quenched into ice brine.

Plate specimens of size $4\times7\times1.5mm^3$ for hardness test were solution-treated and aged at given aging temperatures for up to 50000min. The hardness measurements were made on the heat-treated specimens using a micro-Vickers hardness tester with a 300gf load and a 10sec holding time. Vickers hardness results were obtained as the average values of five measurements.

Powders for X-ray diffraction, that passed through a 330-mesh(45㎛) screen, were produced by using a rotating diamond disk. These powder specimens were vacuum-sealed in a silica tube, and then were subjected to heat treatment. X-ray diffraction studies were carried out on the heat-treated powder specimens using an X-ray diffractometer(Rigaku Denki Co. Ltd., D/Max-2400, Japan). The X-ray diffractometer was operated at 40kV and 50mA. A nickel-filtered Cu $K\alpha$ radiation was used as an incident beam.

Plate specimens for scanning electron microscopic observation, energy dispersive spectroscopy were heat-treated, 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 20kV using a scanning microscope(JEOL, JSM-5400, Japan) equipped with an energy-dispersive system (NORAN, 648B-1SSS, USA).

RESULTS

Hardness test

Isothermal age-hardening curves of this alloy are shown in Fig. 1. The results of the isothermal aging in the 350~450℃ temperature range showed a similar tendency in the changes. The hardness increased markedly at the initial stage of aging and then continued to increase gradually for the time. After showing peak hardness, the hardness decreased drastically and then continued to decreased slowly. The initial hardening was most marked at 350℃, the softening occurred most rapidly and the hardness during the overaging period was lowest at 450℃.

X-ray diffraction study

To elucidate how the supersaturated single phase changes into the stable phases during isothermal aging, X-ray diffraction patterns were taken from the powder specimens solution-treated and aged for the various ranges of time at given aging tempera-

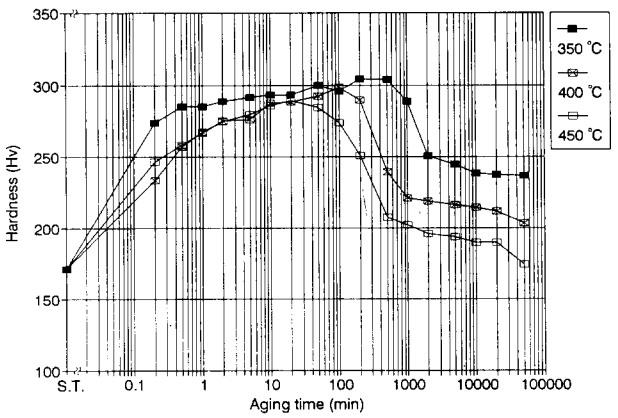

Fig. 1. Isothermal age-hardening curves of this alloy at 350~450℃

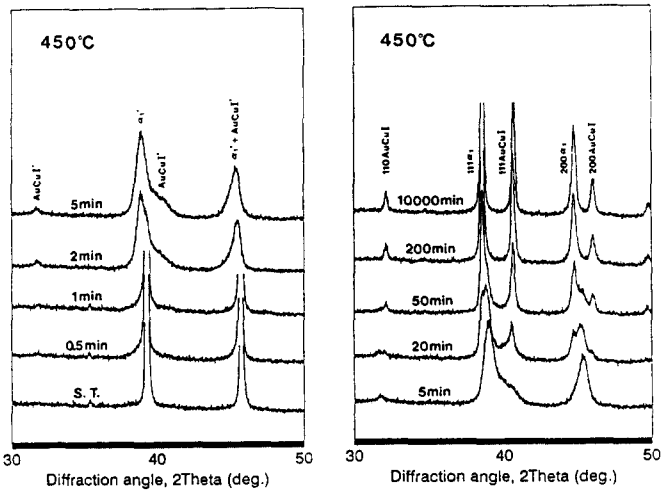

Fig. 2. Changes in the X-ray diffraction pattern during isothermal aging at 450℃

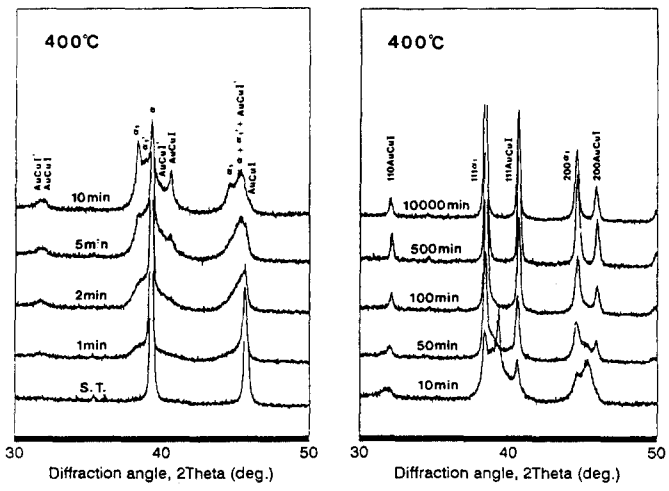

Fig. 3. Changes in the X-ray diffraction pattern during isothermal aging at 400℃

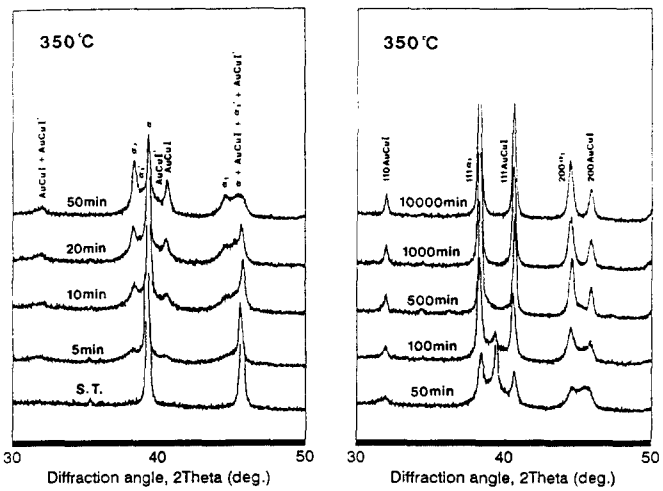

Fig. 4. Changes in the X-ray diffraction pattern during isothermal aging at 350℃

tures. Figs. 2, 3, 4 represent the phase changes at 350~450℃ for the periods indicated.

The α single phase of the solution-treated specimen, which was fcc in structure, was finally transformed into the co-existence of the AuCu I ordered phase with a fct structure and the Ag-rich α_1 phase with a fcc structure by aging at 350~450℃. And the metastable Ag-rich α_1' phase and the metastable AuCu I' ordered phase were formed from the α phase prior to the final formation of the equilibrium Ag-rich α_1 phase and the equilibrium AuCu I ordered phase. However, the sequences of phase changes during isothermal aging were slightly different.

By aging at 450℃, the 111 diffraction peaks of the metastable Ag-rich α_1' and AuCu I' ordered phases were separated, while the 200 diffraction peaks of both phases were superimposed as seen in Fig. 2. This means that the metastable AuCu I' ordered phase has the fct structure with a lattice parameter α similar to that of the metastable Ag-rich α_1' phase with a fcc structure. And the diffraction peaks of the metastable Ag-rich α_1' phase and the equilibrium Ag-rich α_1 phase have a low diffraction angle in comparison with those of the α phase and the metastable Ag-rich α_1' phase respectively. This can be explained as follows. By the formation of the metastable AuCu I' ordered phase in the α phase and the equilibrium AuCu I ordered phase in the metastable Ag-rich α_1' phase, Au and Cu atoms drain out of the parent matrix and the metastable matrix. The atomic size of copper is particularly smaller than those of the other atoms. Consequently, the position of the diffraction peaks of the the metastable Ag-rich α_1' phase and the equilibrium Ag-rich α_1 phase move to the low diffraction angle as a result of the lattice parameter changes.

As can be seen in the diffraction pattern of the specimen aged at 450℃ for 20min(Fig. 2), the 111 reflections of the metastable α_1' and equilibrium α_1 phases and the 110 reflections of the metastable AuCu I' and equilibrium AuCu I phases are clearly separated at 450℃. By aging at the lower temperatures, however, these reflections become superimposed

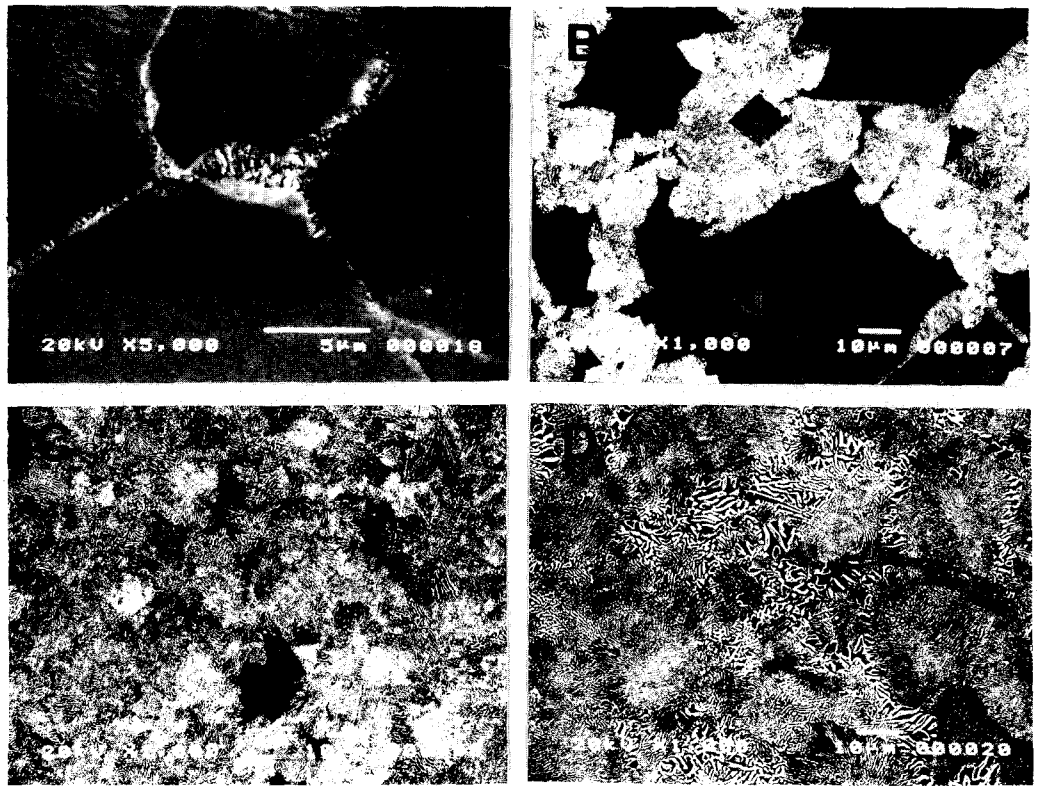

Fig. 5. Scanning electron micrographs of the specimens aged at 450℃ for 20min(A), 200min(B), 500min(C) and 50000min(D). Pyramidal impressions were made witha 25g load.

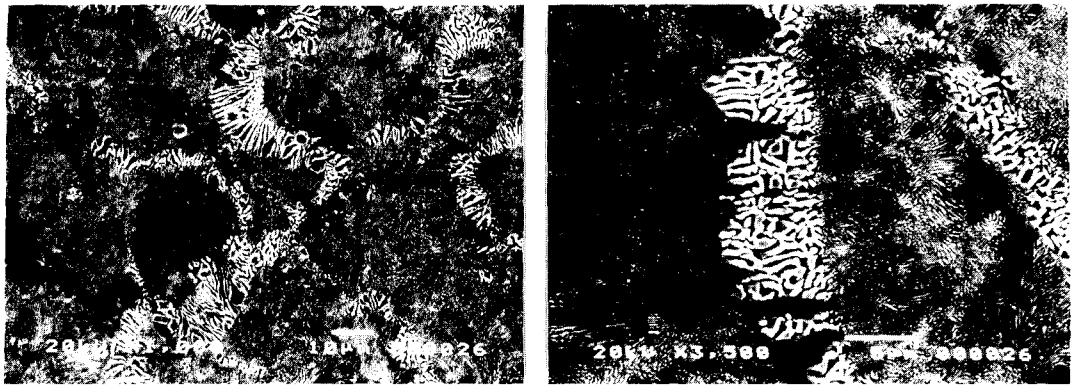

Fig. 6. Scanning electron micrographs of the specimens aged for 50000min at 400℃(A) and 350℃(B)

(Figs. 3, 4). The phase transformation sequence at 450℃ is α → metastable Ag-rich α_1' + metastable AuCu I' and then Ag-rich α_1' + AuCu I' → equilibrium Ag-rich α_1 + equilibrium AuCu I, but the phase transformations at 400℃ and 350℃ proceed by the continuous change of α → metastable Ag-rich α_1' + metastable AuCu I' → equilibrium Ag-rich α_1 + equilibrium AuCu I.

An initial change during aging is a shift of the diffraction peaks of the α phase. The diffraction peaks of the α phase of the specimen aged at 350℃ exhibits the most apparent shift than those of the specimens aged at the higher temperatures. And the diffraction peaks of the metastable Ag-rich α_1' and AuCu I' phases show an apparent shift during the early stage of the transformation of the metastable phase to the equilibrium phase. This can be seen in the 111 reflection of the α_1' phase and the 110 reflec-

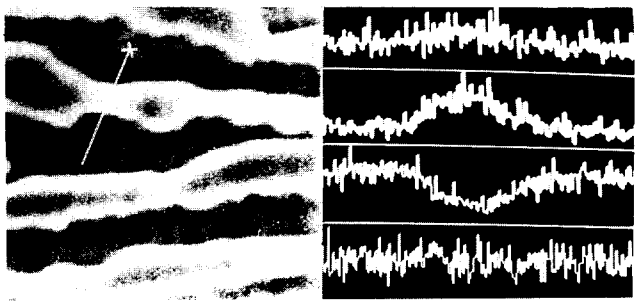

Fig. 7. The variations of element concentration across lamellar structures of the specimens aged at 450℃ for 50000 min. Each of the traces represents Pd(top), Cu, Ag and Au(bottom) respectively.

tion of the AuCu I' phase of the specimens aged at 450℃ for between 5min and 20min(Fig. 2)

SEM observation

Fig. 5 is scanning electron micrographs obtained from the specimen aged at 450℃ for 20min, 200min, 500min and 50000min, respectively. By the isothermal aging, precipitates were initially formed at grain boundaries and grew into the grain interior with increasing aging time. The precipitates were constructed of alternating lamellae.

Pyramidal impressions were made with a 25gf load on the precipitates and the grain interior(Fig. 5(B)). The pyramidal impression of the precipitates is larger than that of the grain interior. This suggests that the softening is caused by the the precipitation of a lamellar structure. Following prolonged aging, the grain interior became almost covered with the precipitates of the fine lamellar structure finally, and then the fine lamellar structure tended to coarsen into larger particles. However, there is a significant difference in the rate of coarsening according to aging temperature. The rate of coarsening increased with increasing aging temperature, as observed in the scanning electron micrographs of the specimens aged for 50000min at 450~350℃(Figs. 5(D), 6).

EDS

Energy dispersive spectroscopy was made to confirm the distribution of each of four elements in the lamellar structure. EDS profiles of the specimens aged at 350~450℃ for 50000min demonstrated that two distinct layers of lamellar structure are Ag-rich, and Cu-, and Pd-rich respectively, and that gold is distributed evenly. Fig. 7 shows the EDS profiles taken from the specimen aged for 50000min at 450℃.

DISCUSSION

Hardness increase

The hardness of the present alloy increases markedly at the initial stage of aging and then maintains a gradual increase in hardness during the early aging period as seen in the isothermal age-hardening curves (Fig. 1). This increase in hardness occurred before a pronounced structural change was observed in the scanning electron microscopic observations. Therefore, some changes in the grain interior are assumed.

Yasuda et al.[2] reported that the initial hardening in the alloy (39.8at.% Au - 27.4at.% Ag - 25.3at.% Cu - 7.6at.% 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 that the hardening was depressed by a relaxation of the strain.

In the present alloy, metastable phases were formed prior to the formation of equilibrium phases. And the shift of the diffraction peaks of the α phase, and the metastable Ag-rich α_1' and AuCu I' ordered phases occurred during hardening. This shift is resulted from the lattice distortions caused by variation in composition of these phases, and provides evidence against a homogeneous mechanism in the transformation. In most systems the final stable phases have such different crystal structures that it is impossible to form coherent interfaces and homogeneous nucleation is then impossible. However, it is often possible to form a coherent nucleus of the metastable phase[7]. And if the product phase has the same crystal structure and a similar lattice parameter to the parent phase, the two phases can form coherent interfaces.

From the results of the isothermal age-hardening and the phase transformation, it can be considered that the age-hardening was mostly attributed to the lattice distortions of the supersaturated α phase resulting from the transformation to the metastable

phases, and was also attributed to the lattice distortions resulting from the transformation of the metastable phases to the equilibrium phases.

The shift of the diffraction peaks of the α phase resulting from the transformation to the metastable phases became more apparent with decreasing aging temperature in the 350~450℃ temperature range. Therefore, the initial hardening was most pronounced at 350℃. A homogeneous mechanism is made easier by a drop in temperature[5].

Hardness decrease

The drastic decrease in hardness occurred after showing peak hardness by prolonged aging. This overaging with softening coincides with the broadening of the precipitates of the lamellar structure, as shown in the scanning electron micrograph of the specimen aged at 450℃ for 200min(Fig. 5(B)). This implies that the softening was attributed to the formation and continuous growth of the precipitates of the lamellar structure. And it could be inferred that the softening by the precipitation at grain boundaries depresses the hardening by the change in the grain interior.

The overaging was accelerated with increasing the aging temperature. At high temperature, softening occurs rapidly due to rapid diffusion. After the drastic decrease in hardness a slow decrease in hardness followed. The hardness of the specimen aged at higher temperature is lower than that at lower temperature during the mild softening. This mild softening coincides with the coarsening of the lamellar structure, as seen in the scanning electron micrographs (Figs. 5 (D), 6). The coarsening leads to a reduction of the surface at the interfaces of the adjacent lamellae. Consequently, it can be thought that the coarsening of the lamellar structure contributed to the mild softening occurred after the drastic softening.

Yasuda et al.[2] reported that the formation of the lamellar structure at grain boundaries by prolonging the aging time, which consisted of the equilibrium AuCu I ordered and Ag-richα_1 phases, did not contribute to the age-hardening. According to Udoh et al.[3], the mechanism of the overaging in the same alloy that Yasuda et al. used was interpreted as a loss of coherency at the interfaces of the adjacent lamellae.

In the present alloy, the formation of the AuCu I ordered phase and the Ag-richα_1 phase which were the stable phases was confirmed by the X-ray diffraction study. And two alternating layers of the lamellar structure which was formed by prolonging the aging time were Ag, Au-rich and Au, Cu, Pd-rich respectively, as seen in the EDS profiles(Fig. 7). This result obtained from the EDS profiles agree well with the result in the 13 carat gold commercial dental Au-Ag-Cu-Pd alloy[6]. From the above results, it can be thought that the lamellar structure composes of the AuCu I ordered phase containing Pd and the Ag-richα_1 phase containing Au.

The compositional boundary of the present alloy exists in the co-existence region of the Ag-richα_1 phase and the Cu-richα_2 phase, or the Ag-richα_1 phase and the AuCu II ordered phase at 350℃ in the suggested isothermal section of the Au-Ag-Cu ternary system[9]. Thus, it could be supposed that the transition temperature of AuCu I ordered structure is raised with the addition of palladium[10,11].

CONCLUSION

The relationship between the isothermal age-hardening behavior and the phase transformation in the commercial dental Au-Ag-Cu-Pd alloy was investigated by means of hardness test, X-ray diffraction study, scanning electron microscopic observation and energy dispersive spectroscopy. The following results were obtained.

By the isothermal aging at 350~450℃, the hardness increased markedly at the initial stage and then continued to increase gradually for the time. After showing peak hardness, the hardness decreased drastically and then continued to decreased slowly.

The age-hardening was mostly attributed to the lattice distortions of the supersaturated α phase resulting from the transformation to the metastable phases, which were more distinct at lower aging temperature. The lattice distortions resulting from the transformation of the metastable phases to the equilibrium phases also made a contribution to the age-hardening.

The overaging with softening was attributed to the formation and growth of the lamellar structure. The

initially drastic softening was due to the broadening of the fine lamellar structure into the grain interior, and the secondly mild softening was due to the coarsening of the lamellar structure which was composed of the AuCu I ordered phase containing Pd and the Ag-richα_1 phase containing Au.

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=국문초록=

시판 치과용 Au-Ag-Cu-Pd합금의 등온시효경화와 상변태 과정과의 관계를 경도시험, X선회절실험, 주사전자현미경관찰, 에너지분산X선분광법으로 연구하여 다음과 같은 결과를 얻었다.

용체화처리된 합금은 350~450℃에서 등온시효처리에 의해, 경도가 시효개시와 함께 신속히 상승하고 일정기간 완만히 증가했다. 그 후, 경도는 급격히 하강하고나서 서서히 저하하였다.

경도의 상승은 과포화고용체(α) → 준안정상(Ag-richα_1' + AuCu I') → 안정상(Ag-richα_1 + AuCu I)의 변태과정에서 생기는 격자 뒤틀림에 기인하였다. 모상(α)의 격자 뒤틀림은 낮은 시효온도에서 현저하였다.