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Effects of Zn addition to AuCu on age-hardening behaviors at intraoral temperature

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The effect of Zn addition to AuCu on the age-hardening rate at the intraoral temperature was investigated to find out the proper condition for high age-hardening rate. The increase in hardness of Zn-added alloys during aging at 37 °C was due to the atomic ordering. With an increase in Zn concentration, hardness of a sample under the as-quenched condition decreased, but the age-hardening rate obviously increased. When Zn content was fixed, a higher solution treatment temperature was more effective for the age-hardening at 37 °C. It was suggested that the formation energy of a vacancy considerably decreased with an increase in Zn content. It is reasonable to consider that the amount of quenched-in excess vacancies are markedly increased with an increase in Zn content when the solution treatment temperature was fixed. By transmission electron microscopic observations, it was revealed that the formation of the AuCu II superstructure contributed to the age-hardening at 37 °C in the high zinc content alloy.

1. Introduction

The addition of a third element to an equiatomic AuCu may change the age-hardening rate of an alloy. Especially when the element having a low melting point is added to the equiatomic AuCu alloy, age-hardening can occur at low temperatures such as intraoral temperature. This implies that if such an alloy is used as a dental alloy, it will become harder in the oral cavity as time goes by. Ohta *et al*. [1] found that the addition of Ga, Al or Zn to AuCu improved the low-temperature age-hardenability. Ouchida *et al*. [2] reported that the age-hardening rate at 37 °C in Au-Cu-Ga alloys increased by increasing the gallium content. However, the relation between the zinc concentration and the age-hardenability at the intraoral temperature of Au-Cu-Zn ternary alloys is unknown. The structural change occurring by Zn addition to AuCu during ordering at 37 °C is also not yet reported. The purpose of this study is to investigate the effect of Zn addition to AuCu on the age-hardening rate at the intraoral temperature and to find out the proper condition for high age-hardening rate at the intraoral temperature.

2. Materials and methods

The compositions of alloys used in the present study were an equiatomic AuCu with the addition of 0, 0.67, 2.03, 5.43, 9.80 and 19.61 at% Zn as listed in Table I. Plate samples, $5 \times 7 \times 0.5\,mm^3$ in size, were solution-treated at 500 °C, 600 °C, 700 °C or 800 °C for 30 min and rapidly quenched into ice brine. They were then aged in a drying oven at a regulated temperature of 37 °C. The hardness was determined with a Vickers microhardness tester with a load of 300 gf and dwelling time of 10 s. The average hardness number was obtained from five indentations. The electrical resistivity measurement was made by a four-terminal potentiometric method with a direct current of 100 mA while the specimens were dipped in a silicone oil bath regulated at 37 °C. The electrical resistivity change during continuous heating at a rate of 1 °C/min was also measured. To determine solidus and liquidus temperatures, differential thermal analysis was done with a heating and cooling rate of 10 °C/min. For X-ray diffraction study, powder specimen which passed through a 200-mesh screen was obtained by filing. They were quenched into ice brine from various temperatures to examine the structural changes by X-ray diffractometer (RAD-rA, Rigaku Corp., Tokyo, Japan) which was operated at 45 kV, 130 mA. As an incident beam, CuK_α radiation was used. A nickel filter was set in front of a receiving slit to cut the CuK_β radiation. For transmission electron microscope (TEM) study, disks of 3 mm in diameter were punched out of sheet specimens of 0.1 mm thickness after the above mentioned solution treatment. After the aging in a 37 °C drying oven for 10 days, they were electrolytically thinned by a double-jet technique in a solution of 35 g of CrO_3, 200 ml of CH_3COOH and 10 ml of H_2O to obtain thin foil specimens for TEM observations. A transmission electron microscope (H-800, Hitachi Co, Tokyo, Japan) was equipped with a specimen-tilting device and installed at Nagasaki University School of Dentistry.

TABLE I Chemical compositions of alloys used (analyzed values)

Alloys	Composition (at%)		
	Au	Cu	Zn
A	49.48	50.52	0
B	49.60	49.73	0.67
C	49.01	48.96	2.03
D	47.33	47.24	5.43
E	45.08	45.12	9.80
F	40.24	40.15	19.61

3. Results

3.1. Age-hardening behaviors

Fig. 1 shows the effects of Zn concentration on the age-hardening rate at 37 °C. The magnitude of age-hardenability was expressed in terms of the ratio of the increase in hardness, ΔH, to the initial hardness, H_0. The age-hardening rate apparently increased with increasing the Zn concentration in case the solution treatment temperature was fixed to 500 °C. Changes in hardness were fast in the early stage and then became slow with the passage of time. Such tendency became more intense as raising the solution treatment temperature.

Fig. 2 shows the variation of age-hardening behavior with the solution treatment temperature in the alloy F. When the solution treatment temperature was as low as 450 °C, age-hardening rate at 37 °C was slow even in a high Zn content alloy as seen in Fig. 2. For the alloy F, when the solution treatment temperature is raised from 600 °C to 700 °C, age-hardenability did not continue to improve. On the other hand, for the alloy which contains less Zn, age-hardenability was still improved by raising the solution treatment temperature from 600 °C to higher.

Fig. 3 shows the hardness of the alloy D just after quenching from various temperatures. There was little difference in hardness when the solution treatment temperature was 500 °C and 700 °C, but in the case of the solution treatment temperature being raised to 800 °C, the hardness was greatly raised in the as-quenched state.

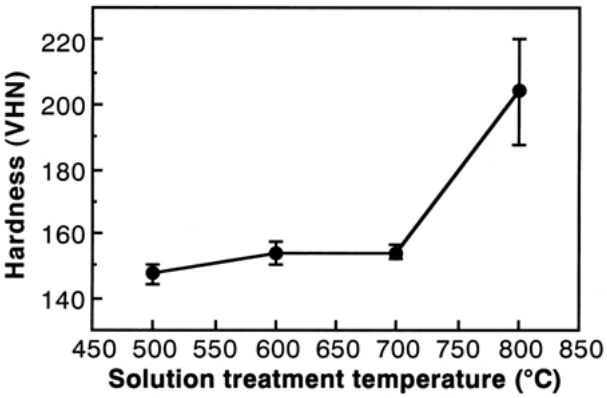

Figure 3 Hardness of the alloy D just after quenching from various temperatures.

3.2. Variations of electrical resistivity

Fig. 4 shows changes in electrical resistivity and hardness with aging time in the alloy E aged at 37 °C. The electrical resistivity value was represented by the ratio of resistivity at any given aging time (ρ_t) to the initial resistivity value (ρ_0). The decrease in electrical resistivity agreed well with the increase in hardness. This suggests that the increase in hardness is due to the atomic ordering. The electrical resistivity of the alloy E decreased for about two weeks during aging at 37 °C, and after that electrical resistivity kept decreasing even though the decreasing rate became slower.

Fig. 5 shows effects of solution treatment temperature on changes of the electrical resistivity in the alloy E aged at 37 °C. It is clear that the decreasing rate of electrical resistivity was much accelerated with increasing of the solution treatment temperature. This suggests that a

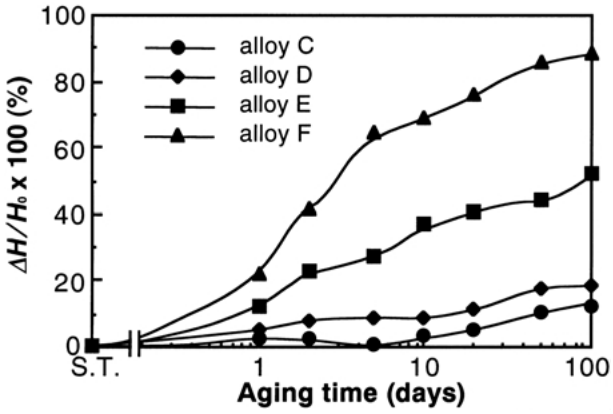

Figure 1 Changes in $\Delta H/H_0$ with aging time of the alloys aged at 37 °C after the solution treatment at 500 °C.

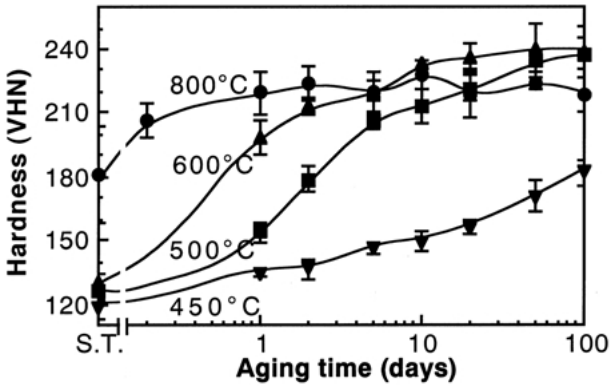

Figure 2 Age-hardening behaviors of the alloy F aged at 37 °C after the solution treatment at various temperatures indicated.

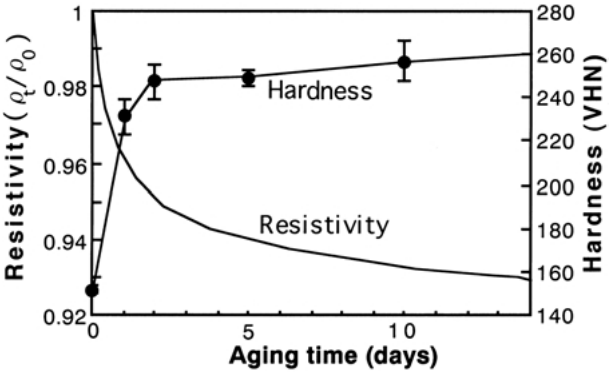

Figure 4 Changes in electrical resistivity and hardness of the alloy E aged at 37 °C after the solution treatment at 700 °C.

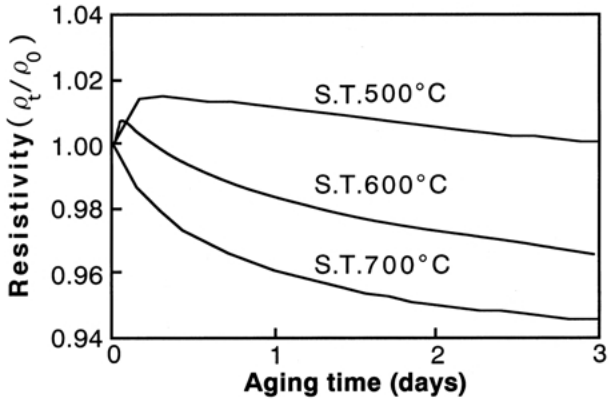

Figure 5 Effect of solution treatment temperature on changes in electrical resistivity of the alloy E aged at 37 °C.

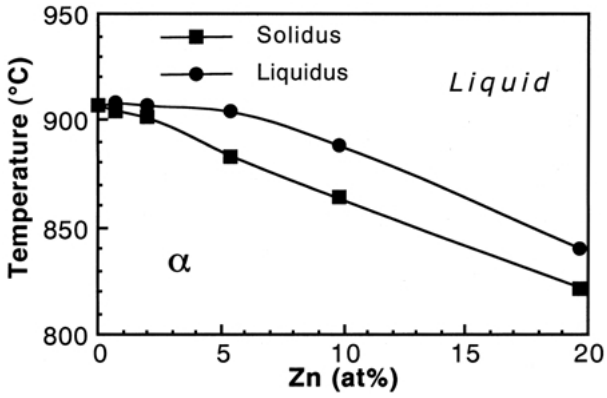

Figure 7 Changes in solidus and liquidus temperatures with Zn content.

higher solution treatment temperature is more effective for age-hardening at a low temperature.

Fig. 6 shows the changes in electrical resistivity at 37 °C with aging time for various alloys. It should be emphasized that the addition of only 0.67 at% Zn to equiatomic AuCu alloy made the electrical resistivity decrease remarkably. A further addition of Zn gradually decreased the amount of electrical resistivity drop.

3.3. Solidus and liquidus temperatures

To investigate the effect of Zn addition to equiatomic AuCu alloy on melting temperature, differential thermal analysis was done. Fig. 7 shows liquidus and solidus curves for the present alloy system determined by differential thermal analysis. Both liquidus and solidus temperatures decreased markedly with increasing the Zn content.

3.4. X-ray diffraction

Fig. 8 shows X-ray diffraction patterns near the 331 and 420 reflections from the α-phase with the variation of solution treatment temperature for the alloy D. Both reflections were sharp when the sample was quenched from 500 °C or 700 °C. On the other hand, these reflections became broad when the sample was quenched from 800 °C. This may be caused by lattice strains due to the atomic ordering during quenching. By Figs 3 and 8, it can be said that the atomic ordering can occur during quenching when the solution treatment temperature is high.

3.5. TEM observation

Fig. 9 shows TEM micrographs taken from the alloy F aged at 37 °C for 10 days after the solution treatment at 700 °C. Fig. 9 (a) is a bright-field (BF) image and (b)–(d) are dark-field (DF) images produced using the 001*x*, 001*y* and 110*z* superlattice reflections respectively. Fig. 9 (e) is the corresponding selected-area electron diffraction (SAD) pattern, clearly showing the formation of the AuCu II-type superstructure. Numerous fine dots with bright contrast in (b)–(d) correspond to fine ordered domains of the AuCu II phase. TEM observations revealed that the AuCu II superstructure formation occurs partially during the age-hardening process at 37 °C in the high Zn content alloy.

4. Discussion

The age-hardening at a low temperature is thought as being under the control of quenched-in excess vacancies. Considering the age-hardening behaviors with the variation of solution treatment temperature in Fig. 2, in case the solution treatment temperature is comparatively low, the age-hardening rate was very slow. This is because the concentration of quenched-in excess

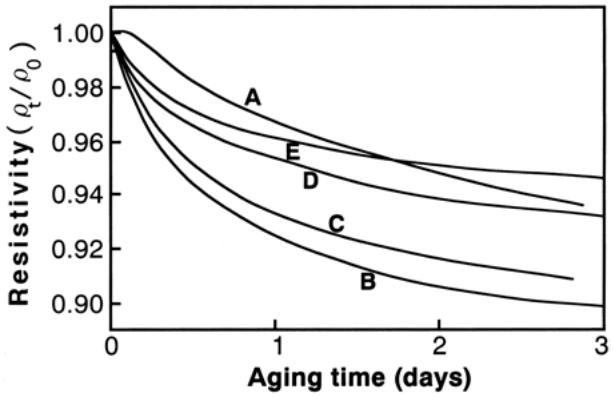

Figure 6 Changes in electrical resistivity at 37 °C with aging time for various alloys after the solution treatment at 700 °C.

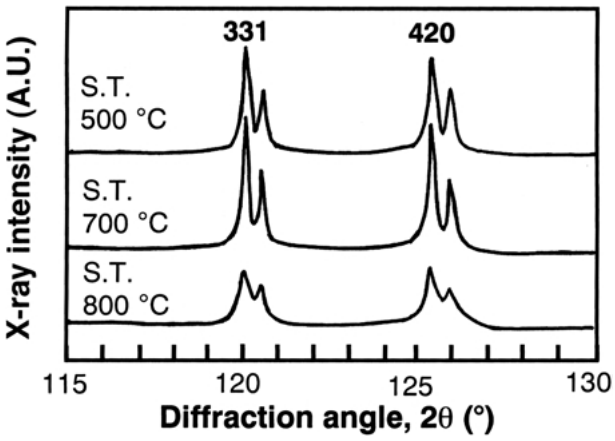

Figure 8 Changes in X-ray diffraction pattern with the variation of solution treatment temperature for the alloy D.

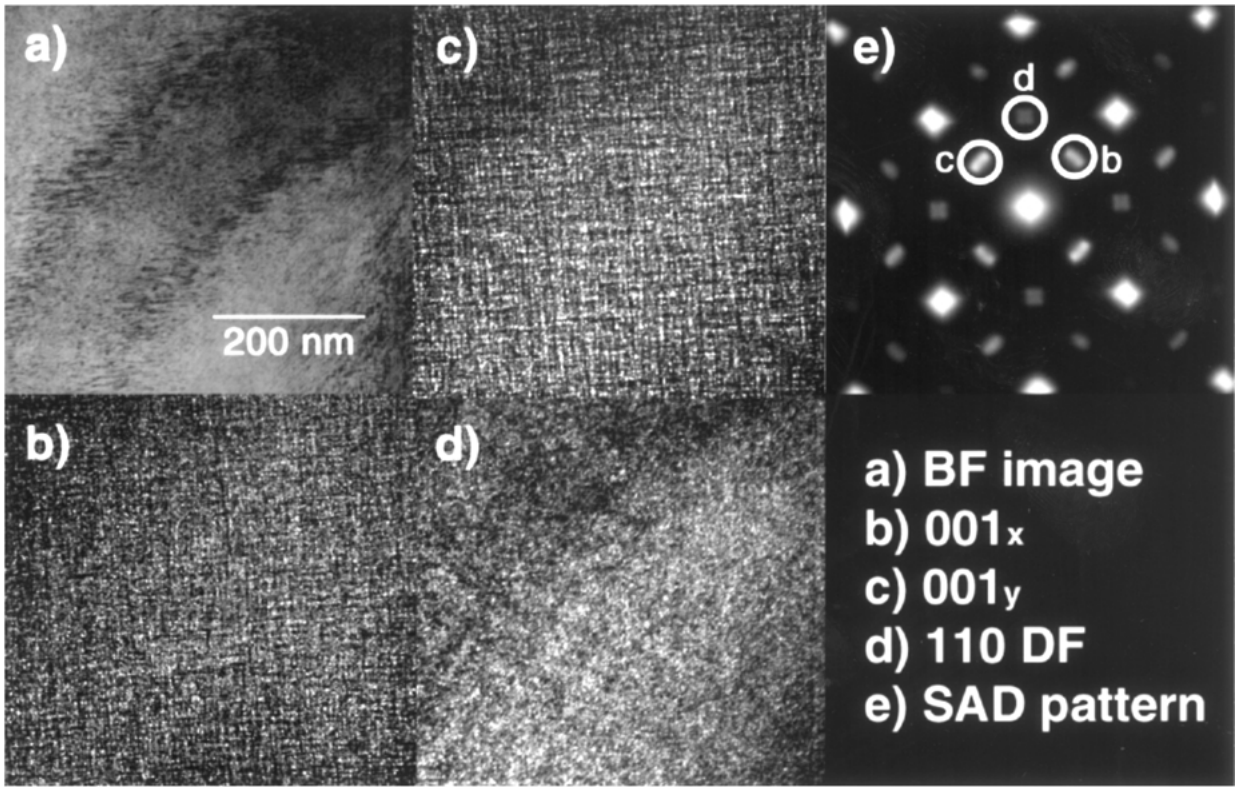

Figure 9 TEM images of the alloy F aged at 37 °C for 10 days after the solution treatment at 700 °C: (a) bright-field (BF) image; (b)–(d) dark-field (DF) images produced using the 0 0 1x, 0 0 1y and 1 1 0z superlattice reflections respectively; (e) selected-area electron diffraction (SAD) pattern.

vacancies is low in the sample quenched from low temperature. Shiraishi *et al*. reported the effect of quenched-in excess vacancies on the low temperature age-hardening in AuCu and Au-Cu-Pd alloys by changing the cooling rate of a sample [3]. According to their results, when the cooling rate of a sample was slow, the concentration of quenched-in excess vacancies considerably decreases. In this event, the age-hardening rate at 37 °C was greatly lowered. Ohta *et al*. [1] investigated the relation between the melting temperature of alloy and the hardening rate at a low temperature, and found that both are closely related. In our study, by raising the solution treatment temperature, the age-hardenability in AuCu-Zn pseudobinary alloys was greatly improved. The above-mentioned controls of solution treatment temperature, the cooling rate of a sample after the solution treatment and the melting point of alloy are all connected with the amount of quenched-in excess vacancies. By keeping the amount of quenched-in excess vacancies high with these controls, age-hardening rate at 37 °C greatly improves. To investigate the effect of Zn addition to AuCu on the concentration of quenched-in excess vacancies, data for the formation enthalpy of a vacancy (H_F) in Au, Cu and Zn was collected. Table II is the list of H_F for each element measured by various methods. It should be emphasized that the formation enthalpy of a vacancy in Zn is considerably lower than that in Au or Cu. This means the addition of Zn to AuCu alloy lets the alloy form vacancies much easily.

The Zn addition to an equiatomic AuCu alloy lowered both liquidus and solidus temperatures of the alloy as seen in Fig. 7. It is known that if added element lowers the melting point of original material, or the liquidus temperature, it will increase diffusion coefficient at any given temperature [9]. The activation energy for vacancy diffusion is linearly proportional to liquidus temperature in Kelvin [2, 9]. Therefore it can be said that the activation energy for vacancy diffusion is brought down by Zn addition and the age-hardenability of AuCu-Zn alloy at low temperature is improved by the decreases in both activation energies for vacancy diffusion and for vacancy formation. The electrical resistivity changes of AuCu-Zn alloys at 37 °C revealed that the age-hardening of these alloys resulted from the atomic ordering. The decreasing rate of electrical resistivity of all alloys was very fast during the early stage of ordering at 37 °C and electrical resistivity kept decreasing even after the passage of about 83 days in the alloy E. Considering these results observed in the AuCu-Zn alloys, it can be said that the ordering of the early stage at 37 °C is assisted by quenched-in excess vacancies and that the ordering of the later stage is thought to have occurred possibly by thermally equilibrium vacancies.

TABLE II The formation enthalpy of a vacancy (H_F) calculated by various methods

Methods	The formation enthalpy of a vacancy (eV)		
	Au	Cu	Zn
Specific heat	1.0 [4]	1.05 [5]	0.61 [6]
Electrical resistivity	0.67 ± 0.07 [7]	0.90 ± 0.05 [7]	0.31 [7]
Positron-annihilation	0.89 [8]	1.42 [8]	0.54 [8]

Numbers in brackets indicate references cited.

In these alloys, with an increase in Zn contents the amount of decrease in electrical resistivity reduced during aging at 37 °C even though the age-hardening rate was increased. Hirabayashi [10] reported that the electrical resistivity of the AuCu II phase is higher than that of the AuCu I phase. Choi *et al*. [11] reported that the Zn addition to the equiatomic AuCu slightly lowered the critical temperature of order-disorder transition but greatly lowered the (AuCu I + AuCu II) coexisting temperature. It was also reported that Zn addition greatly depressed the transformation temperature from disordered Au–Cu phase to AuCu II ordered phase [12]. Considering their reports and our results of TEM study collectively, the reduction of electrical resistivity decrease with Zn addition is interpreted as occurred by the formation of AuCu II phase rather than AuCu I phase as Zn content became higher. From above, the age-hardenability at 37 °C in high Zn content alloy is thought to have occurred by the coherency strain which resulted from the formation of AuCu II-type superstructure formation.

5. Conclusions

The effect of Zn addition to AuCu equiatomic alloy on the age-hardening rate at 37 °C was studied and the following was obtained.

1. The increase in hardness of Zn-added AuCu alloys during aging at 37 °C is due to the atomic ordering.
2. The low temperature age-hardening rate of AuCu alloy obviously increased with the Zn addition. Therefore the addition of Zn to dental alloy is appreciated for the age-hardening in the oral cavity.
3. The effect of solution treatment temperature was great on the age-hardening at 37 °C. The higher the solution treatment temperature, the faster the age-hardening rate at 37 °C, because higher solution treatment temperature is more effective for the formation of quenched-in excess vacancies that contribute to the ordering at low temperature.
4. The age-hardenability of high Zn content alloy is thought to be caused by coherency strains which resulted from AuCu II-type superstructure formation during aging at 37 °C.

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