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Effects of Au/Cu ratio and gallium content on the low-temperature age-hardening in Au–Cu–Ga alloys

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The effects of Au/Cu ratio and gallium content on the low-temperature age-hardening were examined in Au–Cu binary and Au–Cu–Ga ternary alloys by hardness testing, X-ray diffraction and differential thermal analysis. In alloys in which the Au/Cu ratios greatly deviated from the equiatomic one, age-hardenability at 37 °C significantly decreased. Gallium addition lowered the liquidus temperature and increased the age-hardening rate. It is considered that the diffusion rate of the constituents increased with lowering of the liquidus temperature, and that consequently, gallium addition improved the age-hardenability.

1. Introduction

Low-temperature age-hardening is well known to occur in aluminium-based alloys [1]. In dental alloys, high strength together with corrosion resistance and no harmful effects to the patient are required. Shiraishi and Ohta [2] examined age-hardening behaviour of an equiatomic AuCu alloy at 37 °C and reported that the hardness increased with time, the maximum hardness being attained in about 30 days. In a search for dental gold alloys which age-harden at intraoral temperature, Ohta *et al.* [3] investigated the effects of alloying elements on the age-hardenability at 37 °C of AuCu alloy. They found that the addition of gallium to an equiatomic AuCu alloy markedly accelerated the age-hardening rate, and that the hardness of an AuCu–6.0 at % Ga alloy became twice that of the solution-treated alloy after ageing for only one day.

However, realistic chemical compositions of practical alloys are inevitably distant from the equiatomic one, and the effects of gallium addition on the age-hardening behaviour of Au–Cu alloys may vary with the ratio of gold and copper. It is important to know what the effects of the gallium content on the low-temperature age-hardenability in the Au–Cu–Ga alloys might be at various Au/Cu ratios if we are to develop practical dental gold alloys with age-hardenability at intraoral temperature. In this study, the age-hardening characteristics at 37 °C of Au_xCu_{1-x} ($X = 0.40$, 0.45, 0.50, 0.55, 0.60) alloys and various Au–Cu–Ga ternary alloys with different Au/Cu ratios were examined. The effects of gallium substitution for copper in an equiatomic AuCu alloy on the age-hardening behaviour at 37 °C were also examined.

2. Materials and methods

The chemical compositions of the alloys examined are listed in Table I. Specimens were prepared from gold, copper, and gallium of 99.99% purity. These elements were accurately weighed to produce 7 g of each alloy and were melted in a high-frequency induction furnace. The melting was performed in an evacuated quartz tube to prevent oxidation of the molten metal. The ingots thus obtained were hammered at room temperature and homogenized at 700 °C for 3 days. Parallelepiped specimens ($1 \times 3 \times 6$ mm^3) were cut from the homogenized ingots, and were solution treated at 650 °C for 30 min in an argon atmosphere followed by direct quenching into ice–brine. They were polished using a conventional metallographic procedure and then aged in a drying oven at 37 °C. Hardness testing was carried out using a Vickers microhardness tester with a load of 300 gf and a dwell time of 10 s. The average hardness number and standard deviation were obtained from five indentations.

Diffraction specimens, with a particle size smaller than 45 μm, were prepared from Au–Cu binary alloy powders. These specimens were solution treated at 650 °C for 30 min and then aged at 170 °C for 500 h in a vacuum. X-ray diffraction patterns were obtained by using an X-ray diffractometer operated with CuK_α radiation at 50 kV and 80 mA.

The liquidus temperatures of the alloys were determined by differential thermal analysis (DTA). The cubic specimens ($2 \times 2 \times 2$ mm^3) were continuously heated at a rate of 5 °C min^{-1} from room temperature to above the liquidus temperatures in an argon atmosphere.

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TABLE I Chemical composition of alloys used

Specimen	Composition (at %)			Au/Cu ratio
	Au	Cu	Ga	
40AC	40.0	60.0	—	0.667
40AC-2G	39.2	58.8	2.0	0.667
40AC-4G	38.4	57.6	4.0	0.667
40AC-6G	37.6	56.4	6.0	0.667
45AC	45.0	55.0	—	0.818
45AC-2G	44.1	53.9	2.0	0.818
45AC-4G	43.2	52.8	4.0	0.818
45AC-6G	42.3	51.7	6.0	0.818
50AC	50.0	50.0	—	1.00
50AC-2G	49.0	49.0	2.0	1.00
50AC-4G	48.0	48.0	4.0	1.00
50AC-6G	47.0	47.0	6.0	1.00
50AC-Rep2G	50.0	48.0	2.0	1.04
50AC-Rep4G	50.0	46.0	4.0	1.09
50AC-Rep6G	50.0	44.0	6.0	1.14
55AC	55.0	45.0	—	1.22
55AC-2G	53.9	44.1	2.0	1.22
55AC-4G	52.8	43.2	4.0	1.22
55AC-6G	51.7	42.3	6.0	1.22
60AC	60.0	40.0	—	1.50
60AC-2G	58.8	39.2	2.0	1.50
60AC-4G	57.6	38.4	4.0	1.50
60AC-6G	56.4	37.6	6.0	1.50

3. Results and discussion

3.1. Effect of Au/Cu ratio on the low-temperature age-hardening in Au–Cu alloys

Fig. 1 shows the Au–Cu binary equilibrium phase diagram [4]. It is apparent that the AuCuI type superlattice is formed in alloys containing 40–60 at % Au, and that age-hardening of these alloys at a low temperature is attributed to the formation of this superlattice.

According to numerous studies, the driving force for atomic ordering and the ease of atomic diffusion are important factors controlling the rate of ordering in an alloy. It is thought that the driving force for ordering is closely related to the difference in free energy between the ordered and disordered states. At a given low temperature, this difference in free energy is largest at the stoichiometric composition (Au/Cu ratio = 1), and if the composition of an alloy deviates from the stoichiometry, the driving force becomes lower as the deviation increases. On the other hand, the rate of atomic diffusion in an alloy is related to the activation energy, Q_d, for diffusion. Generally, Q_d is the sum of the formation energy, Q_f, and the migration energy, Q_m, of a vacancy. However, for solution-treated specimens, Q_d may be equal to Q_m because such specimens contain a large amount of quenched-in excess vacancies. It is also well known that Q_d is linearly proportional to the liquidus temperature, T_L, of an alloy [5]. That is, at a fixed temperature, the atomic diffusion is easier in an alloy with a lower liquidus temperature.

Fig. 2 shows age-hardening curves of the Au–Cu binary alloys with different Au/Cu ratios aged at 37 °C. The magnitude of age-hardenability of an alloy

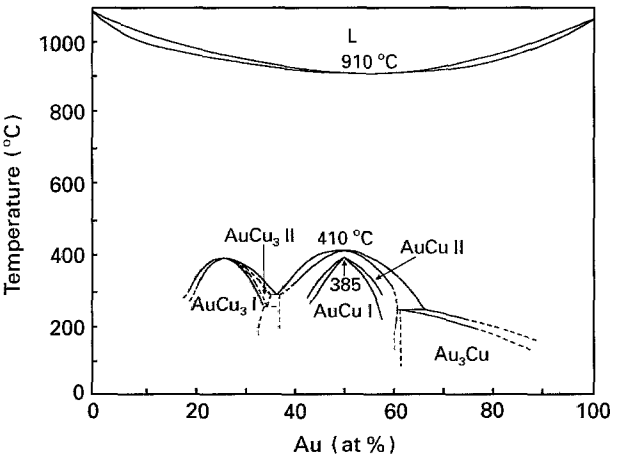

Figure 1 The Au–Cu equilibrium phase diagram redrawn from [4].

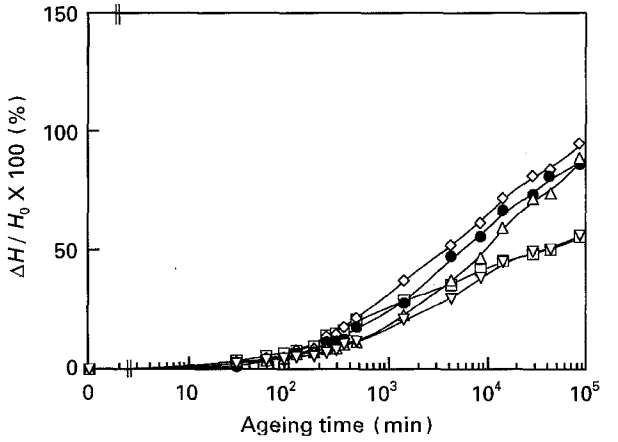

Figure 2 Age-hardening curves of Au–Cu alloys aged at 37 °C: (□) 40AC, (◇) 45AC, (●) 50AC, (△)55AC, (▽) 60AC.

is expressed in terms of the ratio of the increase in hardness, ΔH, to the initial hardness, H_0. Alloys with Au/Cu ratios ranging from 0.818–1.22 revealed almost the same age-hardenability. On the other hand, age-hardenability obviously decreased in alloys in which the Au/Cu ratio deviated greatly from 1.

Fig. 3 shows X-ray diffraction patterns of the Au–Cu binary alloys aged at 170 °C for 500 h. The 0 0 1, 1 1 0 and 2 0 1 superlattice lines from the ordered AuCu I phase were clearly observed in the equiatomic AuCu alloy (50AC). However, the intensities of these lines apparently decreased with the deviation from stoichiometry.

The results shown in Figs 2 and 3 indicate that the rate of ordering, that is the age-hardening rate, decreased with the deviation of the Au/Cu ratio from stoichiometry. Among the presumed controlling factors for the ordering rate, the atomic diffusion rate is not thought to be responsible for the above-mentioned results, because the liquidus temperatures of the Au–Cu binary alloys containing 40–60 at % Au are almost constant, as seen in Fig. 1. It is concluded, therefore, that the decrease in age-hardenability with the deviation of the Au/Cu ratio from stoichiometry is attributable to the decrease in the driving force for ordering.

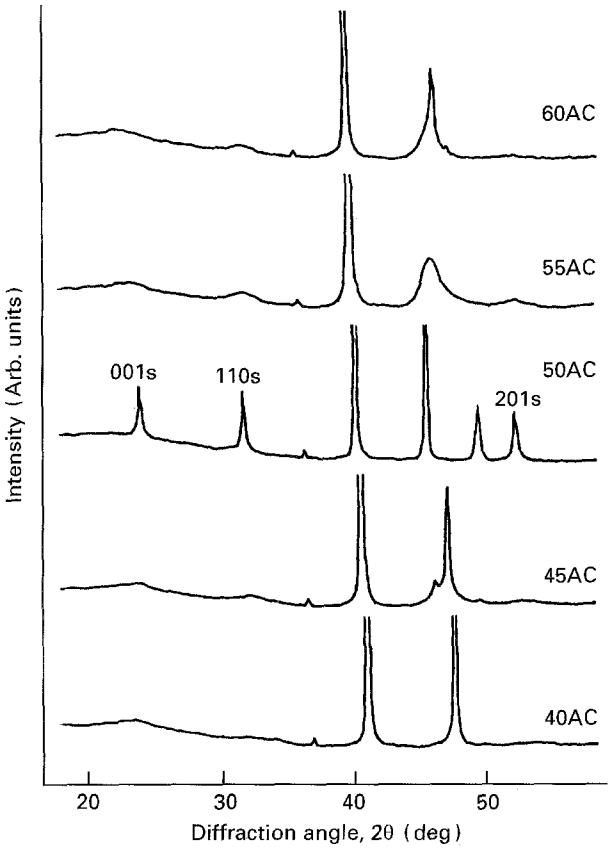

Figure 3 X-ray diffraction patterns of Au–Cu alloys aged at 170 °C for 500 h.

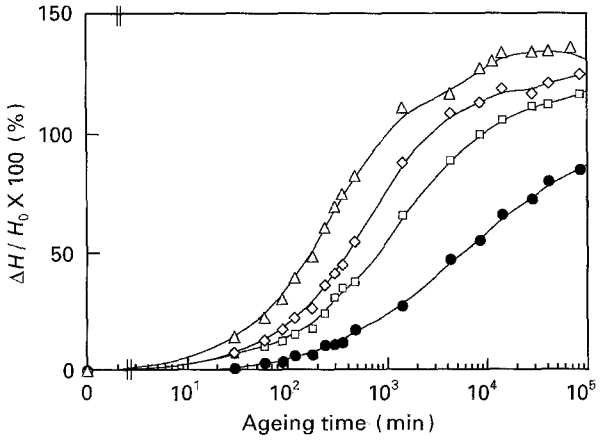

Figure 4 Age-hardening curves of 50AC-G alloys aged at 37 °C: (●) 50AC, (□) 50AC-2G, (◇) 50AC-4G, (△) 50AC-6G.

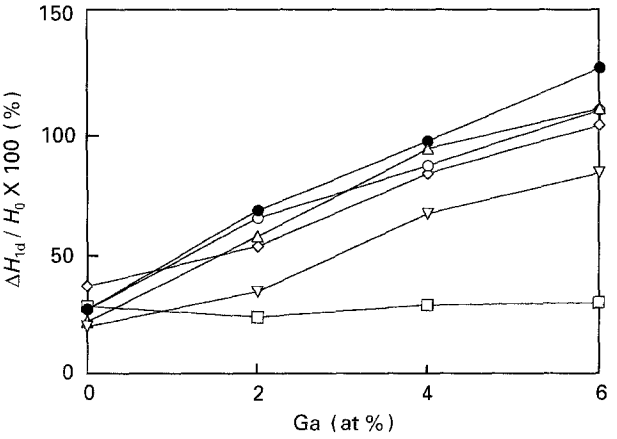

Figure 5 Relation between age-hardening rate and gallium content. Specimens were aged at 37 °C for 1 d: (□) 40AC-G, (◇) 45AC-G, (○) 50AC-G, (●) 50AC-RepG, (△) 55AC-G, (▽) 60AC-G.

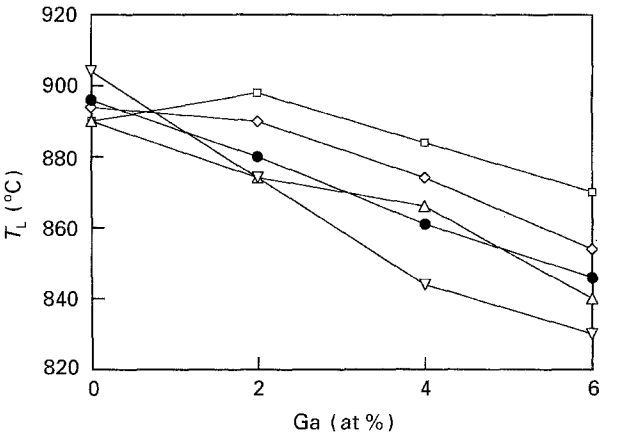

Figure 6 Relation between T_L and gallium content: (□) 40AC-G, (◇) 45AC-G, (●) 50AC-G, (△) 55AC-G, (▽) 60AC-G.

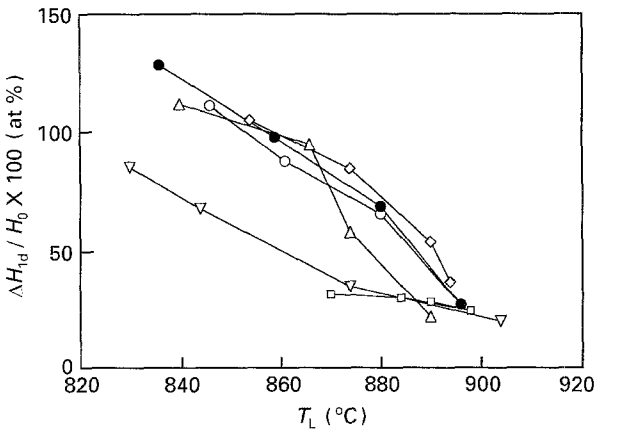

Figure 7 Relation between T_L and age-hardening rate of specimens aged at 37 °C for 1 d: (□) 40AC-G, (◇) 45AC-G, (○) 50AC-G, (●) 50AC-RepG, (△) 55AC-G, (▽) 60AC-G.

3.2. The effect of gallium content on the low-temperature age-hardening in Au–Cu–Ga ternary alloys

Fig. 4 shows age-hardening curves of the Au–Cu–Ga ternary alloys aged at 37 °C. These alloys were made by adding 2–6 at % Ga to the equiatomic AuCu alloy. It is evident from Fig. 4 that age-hardenability increased with gallium content.

Fig. 5 shows the relation between age-hardening rate ($\Delta H/H_0$) after ageing for 1 d, and the gallium content is shown. Age-hardenability increased with gallium content, except for 40AC. The most significant effect of gallium addition was observed in the 50AC-RepG alloy in which part of the copper in the equiatomic AuCu was replaced with gallium.

Fig. 6 shows the relationship between the liquidus temperature, T_L, and the gallium content in the Au–Cu–Ga ternary alloys. The addition of gallium apparently lowered the T_L of the alloys, suggesting

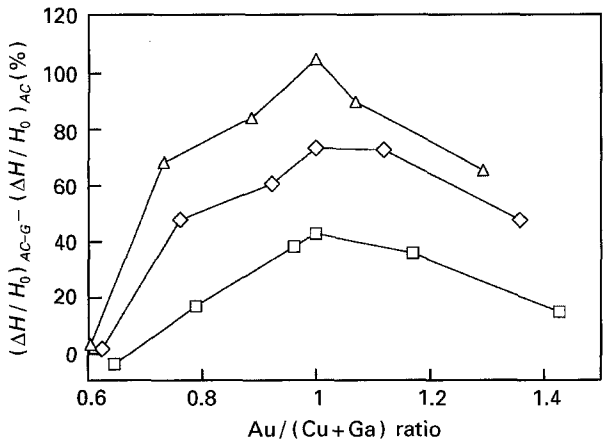

Figure 8 Relation between the Au/(Cu + Ga) ratio and the difference in age-hardening rate between Au–Cu binary and Au–Cu–Ga ternary alloys aged at 37 °C for 1 d: (□) AC-2G, (◇) AC-4G, (△) AC-6G.

that the diffusivities of the constituents at certain temperatures increase with increasing gallium content.

Fig. 7 shows the relationship between T_L and age-hardening rate ($\Delta H/H_0$) after ageing at 37 °C for 1 d. The age-hardenability clearly increased on decreasing T_L. From the results in Figs 6 and 7, it is suggested that gallium addition increases the atomic diffusion rate, resulting in the increase in the age-hardenability. However, the following facts cannot be explained by the above-mentioned mechanism: (1) the greatest improvement of age-hardenability by gallium addition was not attained in the equiatomic alloy, but in the alloy in which part of the copper was replaced with gallium; (2) the age-hardening rate of 40AC-G alloys was low and almost constant regardless of the gallium content.

In Fig. 8, the difference in age-hardening rate between Au–Cu binary ($(\Delta H/H_0)_{AC}$) and Au–Cu–Ga ternary alloys ($(\Delta H/H_0)_{AC-G}$) after ageing for 1d is shown as a function of the Au/(Cu + Ga) ratio. The maximum difference in the age-hardening rate appeared at an Au/(Cu + Ga) ratio of 1. Assuming that gallium atoms occupy copper sites in the AuCu I superlattice, this fact can be well explained. If gallium atoms are taken as copper atoms, the Au/Cu ratio of the 50AC-RepG is invariably unity, while gallium addition to other Au–Cu binary alloys makes the Au/Cu ratio approach or deviate from unity. In the case of a series of 40AC-G alloys, gallium addition shifts the composition from stoichiometry to a position in the composition range where the AuCu I superlattice is not stable. This might be the reason why gallium addition has little effect on the improvement of age-hardenability in the 40AC alloy.

The difference in atomic size is one of the important factors for solute atoms in determining which sublattice they occupy in a superlattice. Comparing the atomic radii of gallium, copper and gold, that of gallium is closer to that of copper than that of gold [6]. Furthermore, assuming that gallium atoms occupy the copper-sites in the AuCu type III superlattice produces a good match between the computer-simulated X-ray diffraction pattern and the measured one [7].

These observations strongly suggest that gallium atoms may occupy the copper sites in the AuCuI type superlattice.

4. Conclusions

The effects of Au/Cu ratio and gallium content on the low-temperature age-hardening in Au–Cu and Au–Cu–Ga alloys were examined by hardness testing, X-ray diffraction and differential thermal analysis. Au_xCu_{1-x} ($x = 0.40, 0.45, 0.50, 0.55, 0.60$) alloys and Au–Cu–Ga ternary alloys containing 2–6 at % Ga with different Au/Cu ratios were prepared. The principal findings are as follows.

1. Age-hardenability of Au–Cu binary alloys at 37 °C decreased in those alloys in which the Au/Cu ratio deviated greatly from the equiatomic one. This is attributed to a decrease in the driving force for ordering as the Au/Cu ratio deviates from stoichiometry.

2. With increasing gallium content, the liquidus temperature of the alloy is lowered and as a result, the age-hardening rate increased. It is considered that the decrease in the liquidus temperature led to an increase in the diffusion rate of the constituents and, as a consequence, improved the age-hardenability.

3. Evidence suggests that in the AuCu I superlattice, gallium atoms preferentially occupy the copper sites.

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