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Dental gold alloys with age-hardenability at intraoral temperature

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Dental gold alloys with age-hardenability at intraoral temperature were developed. Either 3 or 6 at% Ga, Al, Zn, In, Ni or Pd were added to an equiatomic AuCu alloy and the effect of additives on the low-temperature age-hardenability was examined. Alloys containing Ga, Al or Zn exhibited excellent low-temperature age-hardenability. The hardness of an alloy containing 6 at% Ga or 6 at% Al was doubled in one to ten days by ageing at 37 °C. Pronounced hardening was not demonstrated in an as-cast alloy, but solution treatment for only a few minutes provided enough age-hardenability. The age-hardening rate at low temperature related closely with the melting temperature of the alloy. Experimental gold alloys exhibited electrochemical behaviour similar to that of a commercial Type IV gold alloy. It is therefore concluded that AuCu alloy with added Ga, Al or Zn is expected to have enough age-hardenability and corrosion resistance for clinical use in the oral environment.

1. Introduction

Age-hardening is one of the useful properties for dental restorative alloys in regard to controlling their mechanical properties. Age-hardening heat treatment involves solution treatment for softening and ageing treatment for hardening of the alloy. Since these processes are so troublesome, most dental alloys are used in the as-cast state. The chemical compositions of commercial alloys are therefore designed to have enough strength in the as-cast condition. As a result, they usually contain more than four constituents and have complicated microstructures with two or more phases. From the viewpoint of the corrosion resistance, such a complex microstructure has the disadvantage of preferential corrosion of the less-noble phase. If a dental restorative alloy has age-hardenability at intraoral temperature, it is soft enough for occlusal correction and, with the passage of time, becomes hard enough to withstand the occlusion in the oral environment.

The purpose of this study is to develop a single-phase dental gold alloy with age-hardenability at intraoral temperature. Age-hardening in a dental gold alloy is attributed to ordering in the Au–Cu system [1, 2]. We found that an equiatomic AuCu alloy exhibited age-hardening at 37 °C and palladium addition reduced the age-hardenability of this alloy [3]. In this study, elements with low melting point were added to the equiatomic AuCu base alloy and the effect of additives on the low-temperature age-hardenability was examined.

2. Experimental procedure

Chemical compositions of alloys examined are listed in Table I. Six different elements were singly added to the base alloy of equiatomic AuCu. The amount of additive was limited to 6 at % in order to maintain a single-phase structure in the as-cast state, as recommended from the standpoint of corrosion resistivity [4]. Alloys were made from 99.99 or 99.999% pure metals in evacuated quartz ampullae using a high-frequency induction furnace. They were homogenized by alternate cold-working and heating. Homogenized alloys were sliced to a thickness of 1.5 mm, and specimens for hardness testing were cut out of the slices.

The melting temperature of the alloys (the solidus temperature T_m), which was measured by differential thermal analysis (DTA), varied from 784 °C (6Ga) to 928 °C (6Pd). The 6Ga alloy was solution-treated at 650 °C for 30 min, and this temperature corresponded to $0.87T_m$ (K). Consequently, all specimens were solution treated at $0.87T_m$ in flowing argon for 30 min, and

TABLE I Nominal chemical compositions of alloys tested

Specimen	Composition (at %)							
	Au	Cu	Ga	Al	Zn	In	Ni	Pd
3Ga	48.5	48.5	3.0	–	–	–	–	–
6Ga	47.0	47.0	6.0	–	–	–	–	–
3Al	48.5	48.5	–	3.0	–	–	–	–
6Al	47.0	47.0	–	6.0	–	–	–	–
3Zn	48.5	48.5	–	–	3.0	–	–	–
6Zn	47.0	47.0	–	–	6.0	–	–	–
3In	48.5	48.5	–	–	–	3.0	–	–
6In	47.0	47.0	–	–	–	6.0	–	–
AuCu	50.0	50.0	–	–	–	–	–	–
3Ni	48.5	48.5	–	–	–	–	3.0	–
6Ni	47.0	47.0	–	–	–	–	6.0	–
3Pd	48.5	48.5	–	–	–	–	–	3.0
6Pd	47.0	47.0	–	–	–	–	–	6.0

then directly quenched into ice brine to obtain the disordered state.

Ageing treatment was carried out by keeping specimens in a dry oven at 37 ± 0.1 °C. The micro-Vickers hardness was measured just after solution treatment and after appropriate ageing at 37 °C. The hardness number was obtained from the average of five indentations.

To evaluate the chemical stability of the alloys tested, potentiodynamic polarization tests were performed between − 400 and + 1000 mV at a scanning rate of 1 mV s^{-1} in deaerated 1% NaCl solution at 37 °C. The counterelectrode and reference electrode were platinum and Ag/AgCl (KCl saturated), respectively.

3. Results

In Figs 1 and 2, age-hardening curves of alloys containing Ga (Fig. 1) and Al (Fig. 2) are shown with that of a commercial Type IV gold alloy. The results indicate that the Ga- or Al-containing alloy has pronounced low-temperature age-hardenability, but the commercial alloy does not. Fig. 3 shows age-hardening curves of alloys containing 6 at % of additives. The amount of hardening ($\Delta H/H_0$) was expressed as the ratio of the increase in hardness to the initial hardness. It is clear from Fig. 3 that the addition of Ga, Al or Zn promoted age-hardening but addition of Pd decreased the age-hardenability of the AuCu alloy. Addition of Ni had almost no influence on the age-hardenability.

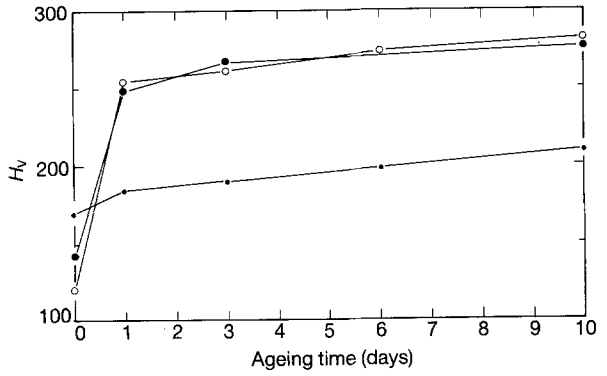

Figure 1 Age-hardening curves of (●) 3Ga, (○) 6Ga and (·) a commercial Type IV gold alloy aged at 37 °C.

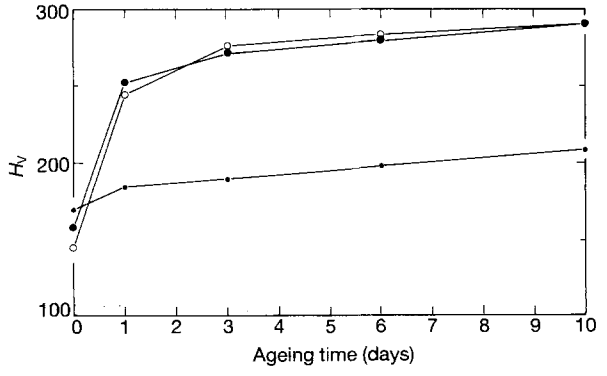

Figure 2 Age-hardening curves of (●) 3Al, (○) 6Al and (·) a commercial Type IV gold alloy aged at 37 °C.

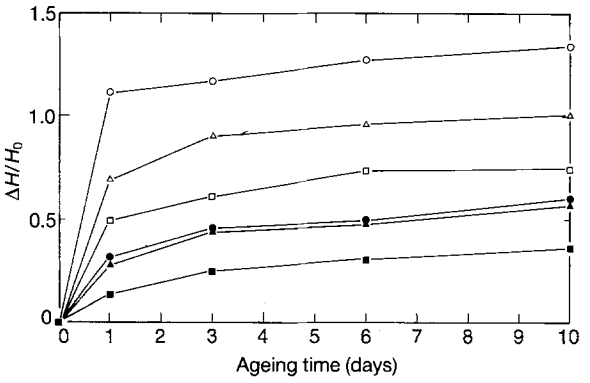

Figure 3 Change in the amount of hardening ($\Delta H/H_0$) of AuCu–6 at % X alloys with ageing time: (○) 6Ga, (△) 6Al, (□) 6Zn, (●) AuCu, (▲) 6Ni, (■) 6Pd.

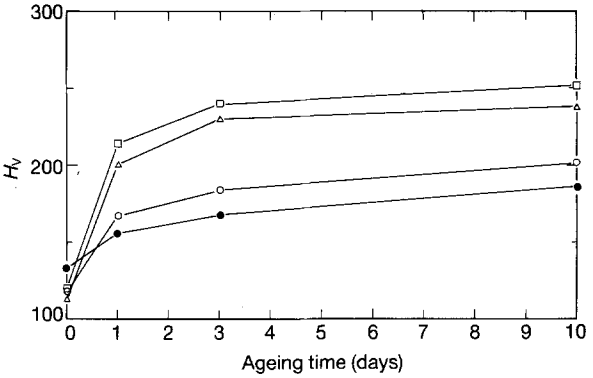

Figure 4 Effect of solution treatment time on the age-hardenability of cast 6Ga alloy: (●) as cast, (○) 0.5 min, (△) 2 min, (□) 4 min.

In Fig. 4, age-hardening behaviours of cast 6Ga alloys are shown. The age-hardening rate of as-cast 6Ga alloy was slow at 37 °C, but heating the cast at 700 °C for only 2 to 4 min and quenching it in room-temperature water provided enough age-hardenability.

Fig. 5 shows anodic potentiodynamic polarization curves of 6Ga, 6Al, 6Zn and a commercial Type IV gold alloy. All the alloys exhibited similar polarization behaviour. The potential at which the current density sharply increases (the critical potential) was higher than 700 mV.

4. Discussion

The age-hardening mechanism of dental gold alloys has been widely studied and is attributed to ordering in the Au–Cu system [1, 2]. Ordering in the AuCu alloy accompanies a structural change from a disordered face-centred cubic lattice to an ordered face-centred tetragonal one. Both structures have four atoms at 0, 0, 0, $\frac{1}{2}, \frac{1}{2}, 0$, 0, $\frac{1}{2}, \frac{1}{2}$, and $\frac{1}{2}, 0, \frac{1}{2}$ in the unit cell. In the ordered state, gold atoms occupy the lattice points 0, 0, 0, and $\frac{1}{2}, \frac{1}{2}, 0$, and copper atoms occupy the remainder. In the equiatomic AuCu alloy, ordering can be easily attained because of the similarity in crystal structures between the ordered and disordered states [5], probably by exchanging atoms between nearest or second nearest neighbours. Some

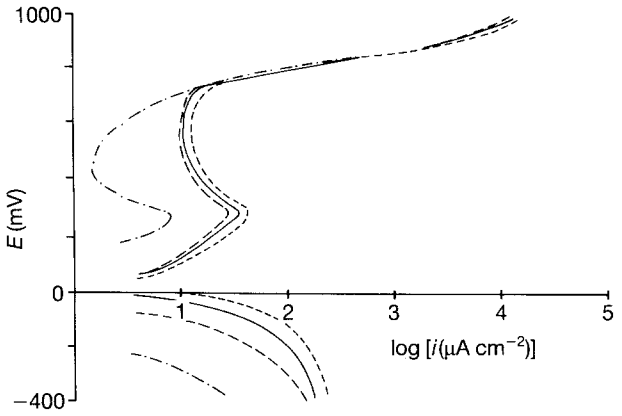

Figure 5 Potentiodynamic polarization curves of alloys tested: (——) 6Ga, (- - -) 6Al, (– –) 6Zn, (– · –) Type IV.

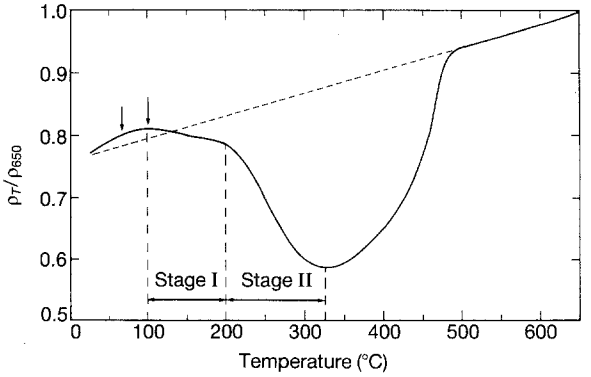

Figure 6 Variation of electrical resistivity for 6Pd alloy during continuous heating at a rate of 1 °C min^{-1}. Arrows indicate the temperatures to which 6Pd specimens were pre-aged.

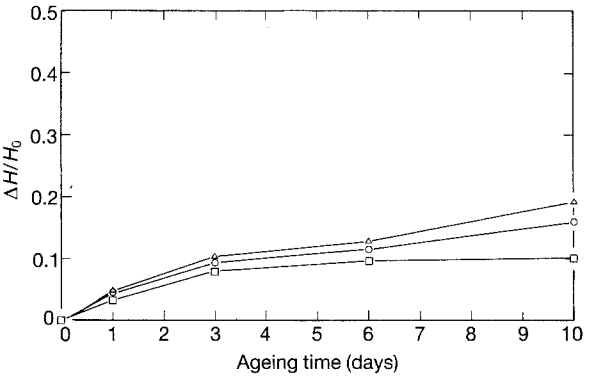

Figure 7 Age-hardening curves of 6Pd alloys solution-treated at 650 °C: (○) no pre-ageing, (△) pre-aged to 70 °C, (□) pre-aged to 100 °C.

amount of long-range ordering is therefore accomplished during quenching, as observed by transmission electron microscopy [3]. Further ordering can be attained by the development of long-range ordered nuclei by the diffusion of atoms, resulting in the generation of an elastic strain field.

Since nucleation and growth are required for the long-range ordering process, the following two factors are thought to relate to the ordering rate of the alloy AuCu–X: the ease of nucleation of long-range ordered domains, and the ease of diffusion. To understand the contribution of the former factor separately, solution-treated 6Pd alloys which showed a low hardening rate were pre-aged from room temperature up to 70 or 100 °C, and then aged at 37 °C. To reduce the probability of nucleation during quenching, the solution treatment temperature was lowered to 650 °C. Since examination of the electrical resistivity change from disordered to ordered states is useful to understand the ordering process, the electrical resistivity change of a solution-treated 6Pd alloy was measured during continuous heating at a rate of 1 °C min^{-1} and the result is shown in Fig. 6. The value of electrical resistivity was normalized to that at 650 °C (the solution treatment temperature). The electrical resistivity increased up to around 100 °C and then decreased through two stages: stage I (100–200 °C) and stage II (200–350 °C). The decreases of resistivity in stages I and II are thought to be accounted for respectively by ordering with the consumption of quenched-in excess vacancies, and by the ordering with the aid of vacancies at equilibrium at a given temperature. Accordingly, continuous heating to 70 or 100 °C will fulfil the condition in which long-range ordered nuclei and excess vacancies coexist. If difficulty in the nucleation of ordered domains is the principal factor in the slow hardening rate of 6Pd alloy, pre-ageing treatment should cause a marked change in hardening rate at 37 °C. In Fig. 7, age-hardening curves for solution-treated and pre-aged 6Pd alloys are displayed. The effect of pre-ageing on the age-hardening curve was not clear, indicating that the low age-hardening rate of 6Pd was not attributed to the difficulty of nucleation.

The above-mentioned result implies that ease of diffusion at low temperature is the most important requisite for age-hardenability at such a temperature. If the diffusion of atoms in the alloy is very slow at low temperature, long-range ordered domains cannot be formed and cannot grow at low temperature and, as a result, the hardening rate is so slow that the alloy cannot be put into practical use. Marinkovic and Simic [6] investigated the reaction kinetics of compound formation at room temperature in thin-film couples of gold and other metals, Au–X. They found that the reaction was diffusion-controlled and that the following relation existed between the diffusion coefficient and the melting temperature of the metal:

$$D = 3.66 \times 10^{-11} \exp(-0.015 T_t) \quad (1)$$

where D is the diffusion coefficient at room temperature (cm^2 s^{-1}) and T_t is the melting temperature (K) of the other metal X. This equation suggests that a binary gold alloy with an element having a low melting temperature has a high diffusion rate. If the ordering rate at low temperature is controlled by the diffusion of atoms, a higher ordering rate is expected in an AuCu–X ternary alloy containing an element with a low melting temperature, compared with the AuCu binary alloy. To clarify this hypothesis, the initial hardening rate ($\Delta H/H_0$ for the first day of ageing) was plotted in Fig. 8 against the melting temperature (solidus temperature) of the tested alloys AuCu–X. This revealed that the following relationship exists between the low-temperature age-hardening

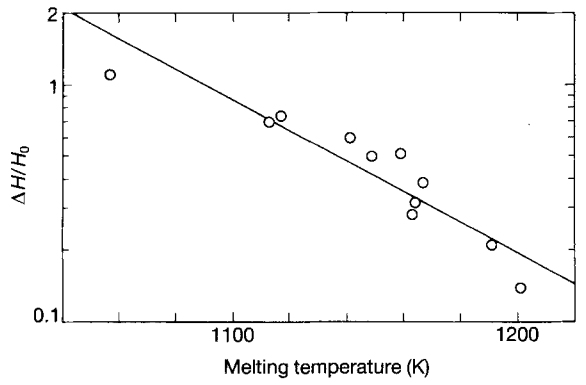

Figure 8 Relation between initial age-hardening rate $\Delta H/H_0$ and melting temperature of alloys.

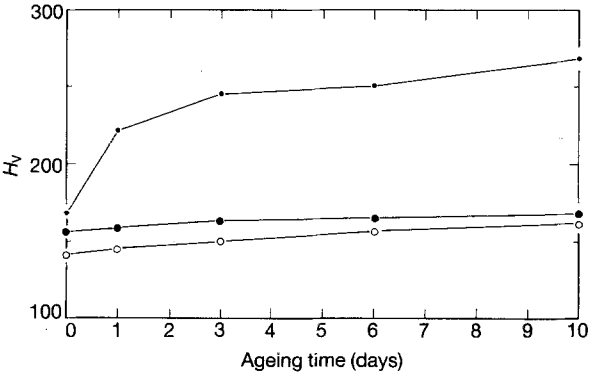

Figure 9 Age-hardening curves of (●) 3In, (○) 6In and (·) AuCu alloys. All alloys were solution-treated at 650 °C.

rate and the melting temperature T_m (K):

$$\Delta H/H_0 = 3.76 \times 10^6 \exp(-0.014 T_m) \quad (2)$$

The similarity between the empirical Equations 1 and 2 strongly suggests that ease of diffusion is the controlling factor for low-temperature ordering in the alloy AuCu–X.

Indium has a low melting temperature (156.4 °C) and is also expected to be an effective additive for low-temperature age-hardening of the AuCu alloy. However, the age-hardenability was remarkably lowered by adding In, as shown in Fig. 9. It is reported that In has a large binding energy with a vacancy and that it traps free vacancies [7]. Therefore, the results in Fig. 9 are attributed to interaction between the additive atoms and vacancies, resulting in a decrease in the number of effective free vacancies for diffusion. This result suggests that a sufficient amount of free vacancies is required for high diffusivity at low temperature.

As shown in Fig. 4, the as-cast alloy 6Ga did not show pronounced hardening at 37 °C. The cooling rate of a casting in a mould is not fast enough for vacancies to be frozen in and a considerable amount of ordering proceeds during cooling, as inferred from the high initial hardness of the as-cast specimen. However, heat-soaking of the casting for only 2 min at 700 °C and quenching it into water provided pronounced age-hardenability. This fact suggests that heating for only 2 min introduced enough vacancies to contribute to the ordering. This heat treatment was carried out by putting the casting in a wax-burnout furnace for 2 min and dipping it into room-temperature water. Such a procedure is not troublesome and is applicable in a dental laboratory.

As seen in Fig. 5, experimental gold alloys exhibited almost similar polarization behaviours to that of a commercial Type IV gold alloy. Their low current density and high critical potential imply a high corrosion resistance of these alloys. It is suggested, therefore, that AuCu alloys with added Ga, Al or Zn possess enough corrosion resistance for clinical use.

5. Conclusions

This investigation was directed toward the development of dental gold alloys with age-hardenability at intraoral temperature. An equiatomic AuCu was chosen as the base alloy and six different elements were singly added.

Addition of Ga, Al or Zn was effective to promote the age-hardenability of AuCu alloy at low temperature. The hardness of an alloy containing 6 at % Ga or 6 at % Al was doubled in one to ten days by ageing at 37 °C. In contrast, addition of Pd lowered the age-hardenability. An element having a high interaction energy with vacancies also decreased the age-hardenability, even though its melting temperature was low. It was concluded that the ease of diffusion at low temperature was the most important factor controlling the low-temperature age-hardening rate, and that the hardening rate related closely with the melting temperature of the alloy.

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