J Mater Sci: Mater Med (2007) 18:577–581
DOI 10.1007/s10856-007-2304-6

Two different types of age-hardening behaviors in commercial dental gold alloys

Kunihiro Hisatsune · Takanobu Shiraishi · Yasuko Takuma · Yasuhiro Tanaka · Rhodora H. Luciano

Received: 17 March 2005 / Accepted: 1 March 2006

Abstract Age-hardening behavior during continuous heating in commercial dental casting gold alloys was investigated by means of electrical resistivity measurements, hardness tests and X-ray diffraction. Two distinguishable behaviors were detected. It is considered that the difference was attributed to the amount of platinum, and the atomic ratio of gold and copper in each alloy. The phase transformations during continuous heating progressed into two steps (stages I and II). Increase of the platinum addition in gold-based alloys retards the rate of the reaction and decreases remarkably the amount of stage I.

1 Introduction

It is well known that dental gold alloys have a complex combination of constituents with five or more elements. The roles of the additional elements in the alloys have been understood imperfectly. In Japan, the addition of platinum in gold-based alloys was met with a favorable reception. Platinum is contributory to the persisting ductility of the alloys after heat treatment. Although Wise *et al.* [1, 2] have reported the role of platinum metals in gold alloys, there has been no experimental evidence of this fact. However, it is very important for us to understand the effect of platinum addition on determining the most acceptable content of dental gold alloys.

Gold alloys with different amount of platinum are utilized in dental clinical treatment. For strengthening, some phase transformation, namely age-hardening is required. The age-hardening mechanisms have already been investigated in some commercial alloys [3–6]. During a study of other gold alloys, we recognized a distinguishable change of phase transformation on the resistivity measurements. Aim of the present study is to clarify the effects of platinum metals addition on classification in commercial dental gold alloys.

2 Materials and methods

Four kinds of commercial dental gold alloys (No. 1: Platinum gold alloy, GC Corp., Tokyo, Japan; No. 2: Super gold Type IV, Shofu Inc., Kyoto, Japan; No. 3: GP Ace 305, Tokuriki, Tokyo, Japan; No. 4: PC-2, Nihonbashi Tokuriki, Tokyo, Japan) were used. The nominal compositions are shown in Table 1. The variations of content of copper or platinum are of interest.

The alloys were firstly solution-treated at 700 °C for 60 min and quenched into iced brine. Thereafter, they had a continuous heating from room temperature to 700 °C at a rate of 0.1°C/min, namely an anisothermal annealing. The aging behavior during the anisothermal annealing was observed by means of electrical resistivity measurements, hardness tests and X-ray diffraction (XRD). The electrical resistivity measurements [7] were made by a four-terminal DC potentiometric method with a constant current of 0.1A at each temperature of about 5 °C intervals in vacuum. The hardness tests were made using a diamond pyramid hardness indenter with a 300 g load. Each hardness value quoted is the average of five indentations. The XRD study was carried out on the filed and appropriately heat-treated powder specimens by using nickel-filtered CuK$_\alpha$ radiation.

K. Hisatsune (✉) · T. Shiraishi · Y. Takuma · Y. Tanaka · R. H. Luciano
Division of Dental and Biomedical Materials Science, Department of Developmental and Reconstructive Medicine, Course of Medical and Dental Sciences, Nagasaki University Graduate School of Biomedical Sciences, Nagasaki 852-8588, Japan
e-mail: hisatune@net.nagasaki-u.ac.jp

Table 1 Nominal compositions of the dental gold alloys used

	Composition, wt% (at%)						
Alloy	Au	Cu	Ag	Pt	Pd	Zn	Atomic ratio (Cu/Au)
Group A							
No. 1	68	16	7	5	3	1	0.73
	(47.2)	(34.3)	(8.8)	(3.5)	(3.8)	(2.0)	
No. 2	70	14	10	1	4	1	0.62
	(48.9)	(30.3)	(12.7)	(0.7)	(5.2)	(2.1)	
Group B							
No. 3	75	11.5	5.5	7	0	1	0.47
	(57.3)	(27.3)	(7.7)	(5.4)	(0)	(2.3)	
No. 4	65	10	16	7	2	0	0.47
	(47.8)	(22.8)	(21.5)	(5.2)	(2.7)	(0)	

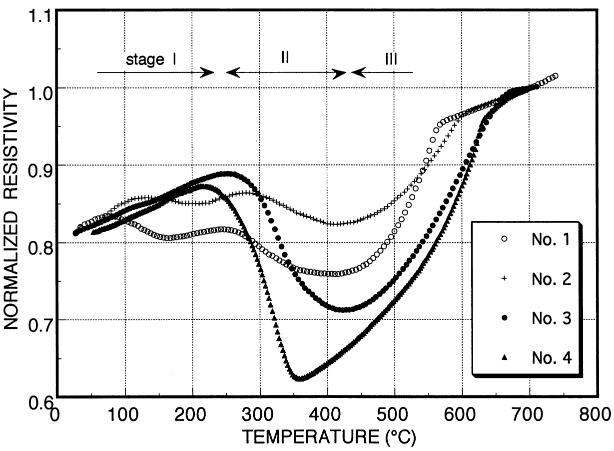

Fig. 1 Resistivity changes with temperature in the dental gold alloys during an anisothermal annealing at 0.1 °C/min

3 Results

3.1 Electrical resistivity changes

Figure 1 shows anisothermal annealing curves of electrical resistivity at a heating rate of 0.1 °C/min in the specimens of Nos. 1–4 after the solution treatment and then quenching. Normalized resistivity (ρ_T/ρ_{700}) is a ratio of the resistivity at each measured temperature (T °C) and that at a solution-treated temperature (700 °C). It is noted that decrease of the resistivity (stages I and II) due to some phase transformations occur in the temperature region between 80 °C and 450 °C depending on the composition of the alloys. After attaining a minimum value, the resistivities increase and a change of the slope is seen at each critical temperature.

Judging from the decrease behaviors in the lower temperature region (80–450 °C), the specimens in the present study are classified in two groups A and B as seen in Table 1. Group A (Nos. 1 and 2) represents two steps change (stages I and II), while group B (Nos. 3 and 4) does one step change (stage II) as seen in Fig. 1. A lack of stage I seems to be recognized in the latter. The decreases of the group A samples tend to be smaller than those of the group B. It is considered that from the similar resistivity studies [8–12], the increase behaviors (stage III) follow the equilibria and the disordering occurs. Each critical temperature of the order-to-disorder transformation is estimated to be 572, 603, 676 and 635 °C for No. 1, No. 2, No. 3 and No. 4 specimens, respectively. It is noted that the critical temperatures in the group A are lower than those in the group B. This is considered to depend on the amount of platinum with higher melting point, as El Araby *et al.* [13] reported that platinum addition in CuAu alloy raised considerably the critical temperature.

3.2 Hardening behaviors

Figure 2 shows variations of hardness with temperature for the specimens Nos. 1 and 3 during an anisothermal annealing at a rate of 0.1 °C/min. The hardness of the specimen No. 3 in group B slowly increases from about 200 °C with a rise in temperature, and reach a peak at about 375 °C and then softening begins. On the other hand, the specimen No. 1 in

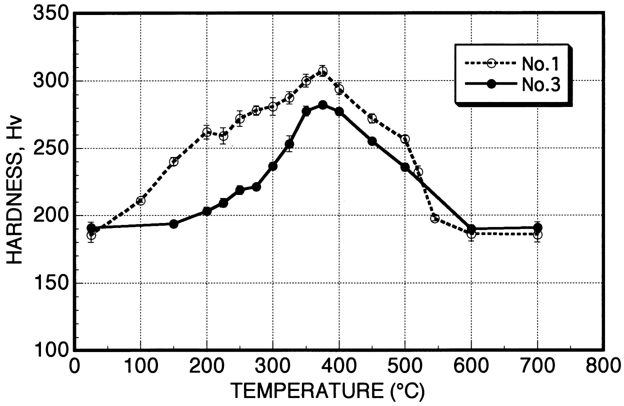

Fig. 2 Variations of hardness with temperature in the dental gold alloys during an anisothermal annealing at 0.1 °C/min

group A already starts to harden at 100 °C. After obtaining an arrest like hardness peak, the hardness further increases and attains an obvious peak at 375 °C followed by softening. The difference of the hardening behavior between the specimens in groups A and B is in good agreement with that of the resistivity. Namely, the former produces two hardening stages (I and II) the latter apparently produces one stage (II). Stage III at higher temperature region corresponds to the softening.

3.3 Crystal structural changes

XRD experiments were performed for Nos. 1 and 3 specimens, because the behaviors of Nos. 2 and 4 were similar to those of Nos. 1 and 3, respectively, on electrical resistivity measurements and hardness tests. Figures 3 and 4 show variations of XRD line profiles at the vicinity of fundamental reflection lines 111 and 200 for the specimens No. 1 and No. 3 respectively during an anisothermal annealing at a rate of 0.1 °C/min. Both specimens solution-treated at 700 °C had a single phase (α_0) with face-centered cubic (fcc) lattice.

No.1 specimen at 150 °C produced a metastable phase with ordered face-centered tetragonal (fct) lattice though not be shown in Fig. 3, which corresponds to stage I. This metastable phase is referred to as $L1_0'$ to distinguish from stable $L1_0$ structure which was detected at higher temperature. We could not distinguish the fundamental reflections (111 and 200) of the ordered phase from those of the matrix fcc phase (α_0) at 200 °C as seen in Fig. 3. However, each reflection line becomes broad as expected from the hardness behaviors. The fundamental lines for the α_0 phase do not change until that at 300 °C. It is noticed that the 200 line for the $L1_0'$ phase is detected at lower angle side of that for the α_0. This reaction corresponds to stage II. The appearance of 200 line from the $L1_0'$ phase depends on the volume fraction and the lattice parameter. There is no additional line in the vicinity of 111 line. At 400 °C, the α_0 phase disappears and the $L1_0'$ phase is observed at both 111 and 200 lines. At the same time, the α_2 (fcc) and the $L1_0$ (fct) as the stable phases can be obviously seen on 111 line. The existence of 200 line from the $L1_0$ phase is not clear because of small amount of the volume fraction. On the way to the stable phases, two kinds of $L1_0$phases were confirmed. As same as Hisatsune *et al.* [5, 14] have reported in a dental gold alloy, it is considered that a metastable phase $L1_0'$ in the grain interior and a stable phase $L1_0$ at the grain boudaries coexist. Then the metastable phase disappears and only the stable phases remain at 500 °C.

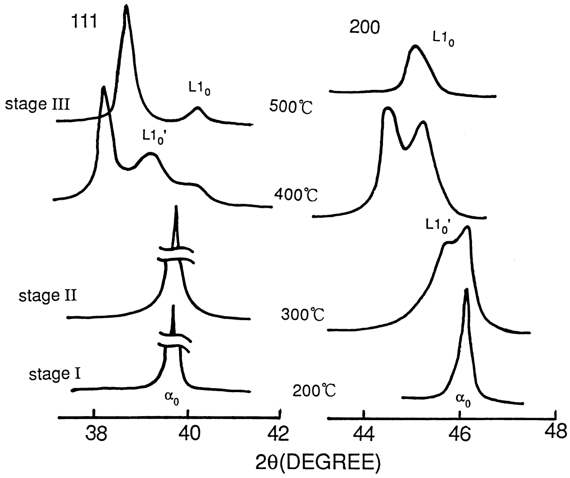

Fig. 3 Variations of XRD line profiles of the specimen No. 1 with temperature during an anisothermal annealing at 0.1 °C/min

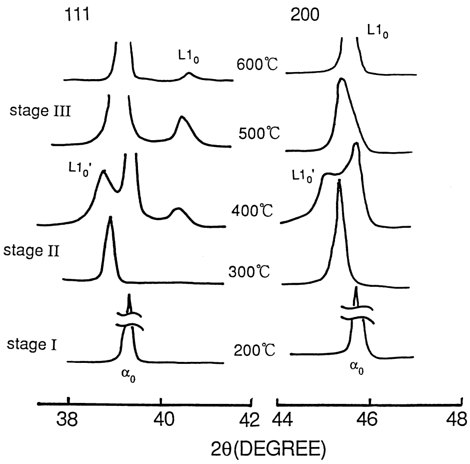

Fig. 4 Variations of XRD line profiles of the specimen No. 3 with temperature during an anisothermal annealing at 0.1 °C/min

On the other hand, at first glance, the XRD line profiles of the specimen No. 3 as can be seen in Fig. 4 seem to be remarkably different from that of the specimen No. 1 in Fig. 3. At 150 °C the $L1_0'$ phase was detected the same as in No. 1 specimen. At 200 °C and 300 °C, both 111 and 200 lines move to the lower angle side. Although the coexistent phases at 400 °C are α_2 (fcc), $L1_0$ (ordered fct) the same as those in No. 1 specimen, each position of the diffraction angle from the three phases is remarkably different. In the case of 111 lines, the $L1_0'$ phase in No. 1 specimen locates between $L1_0$(ordered fct) α_2 and $L1_0$, while that in No. 3 specimen locates at the lowest angle position. This behavior must be due to a difference of lattice parameters for the $L1_0'$ phase. At 500 °C and 600 °C, the α_2 and $L1_0$ remain as the stable phases.

Figure 5 shows variations of the half width from the 331 and 420 fundamental reflection lines with temperature in specimens Nos. 1 and 3. The change in No. 1 specimen occurs faster than that in No. 3 specimen, which is in good agreement with the hardness behaviors as can be seen in Fig. 2.

In any way, the specimens Nos. 1 and 3 does not produce substantially any different crystal structural changes except

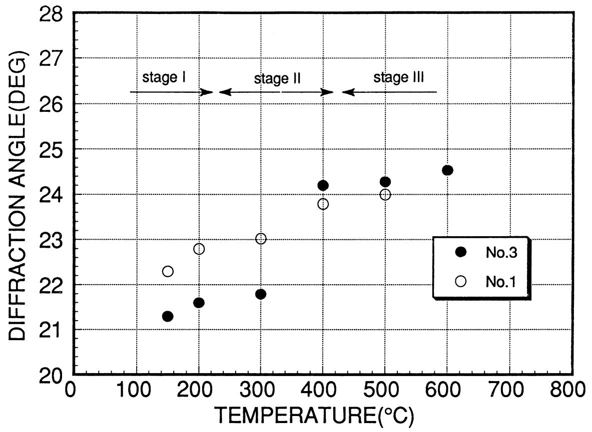

Fig. 5 Variations of the diffraction angle $2\theta_{001}$ from the $L1_0$ phase with temperature in the specimens Nos.1 and 3 during an anisothermal annealing at 0.1 °C/min

the lattice parameters, degree of the line broadening and volume fraction of reaction products. It is considered that both specimens in groups A and B progressed in the same phase transformation process, although each has different reaction rate. The reaction for each stage is identified by the following; stages I and II stage III

$$\begin{aligned}\alpha_0(\text{fcc}) &\Rightarrow L1'_0(\text{ordered fct}) + \alpha_0(\text{fcc})\\ &\Rightarrow L1_0(\text{ordered fct}) + \alpha_2(\text{fcc})\end{aligned}$$

The fct phase with an $L1_0$ structure must base on CuAu I from the composition of the alloys.

4 Discussion

During anisothermal annealing, the dental casting gold alloys in the present study apparently produced one- or two-stages phase transformation depending on the composition, and can be classified into two groups. The alloys with two-stage reaction (group A) tend to harden more easily and have a fast reaction in the lower temperature region. According to the manufacturer's data, it is noted that the elongation of the specimen group B is considerably big even after the hardening heat treatment. This must be a reason why a gold alloy with more platinum is favorable in Japan.

It is very important for us to understand the existence of two different types of age-hardening. There is no difference on the reactions themselves from the XRD data during anisothermal annealing. From the intensity and the diffraction angle of each phase, it is considered that the differences are due to volume fractions and the lattice parameters of each reaction product. It has already been reported by Hirabayashi and Weissmann [15] in binary CuAu alloy, and by Hisatsune *et al.* [5, 14] and Tani *et al.* [6] in dental gold alloys that the hardening at the early stage is due to the coherency strain between a matrix phase with fcc structure and an ordered CuAu I phase with fct structure. The coherency strain in the present alloys may be more effective in the specimen No. 1 than in specimen No. 3, because of much difference in lattice parameter between the matrix and the $L1_0'$ phase in the specimen No. 1. As reported by Hisatsune *et al.* [5, 14] in dental gold alloys, the stages I and II must correspond to the ordering by the migration of quenched-in excess vacancies and of equilibrium vacancies, respectively, followed by a reaction to the equilibrium phases.

As seen in Table 1, the specimens Nos. 1–4 have remarkable variations of composition. One of the big differences is the content of platinum contained in the specimens. Amount of platinum in the group A is smaller than that in the group B. El Araby[16] reported the effect of platinum addition on the ordering in equiatomic alloy CuAu. According to his results of resistivity during anisothermal annealing, the ordering completed in two stages (stages I and II), and stage I decreased and the stage II increased remarkably with increasing the platinum content. The resistivity curve in a CuAu-6.92at%Pt alloy obtained by El Araby [16], resembles that of the specimen No. 1 in Fig. 1. On the other hand, according to Hernandez *et al.* [17] who studied the effect of palladium addition in CuAu alloy by similar resistivity measurements, the decrease of the stage I was not so remarkable as that of platinum. A CuAu-0.96 at%Pt alloy by El Araby[16] and a CuAu-5at%Pd alloy by Hernandez *et al.* [17] seem to be comparable in the resistivity curve. The group B contains considerable platinum more than 5 atomic percentage, while the group A contains small amount of platinum. In the case of the present alloys, palladium may not be effective on the retardation of the ordering judging from the results of Hernandez *et al.* [17]. Furthermore, recently Ohta *et al.*[18–20] reported that the hardening rate in CuAu-X (X = Ga, Al, Zn, Pd) alloys related closely with the melting temperature. Their results reveal that the hardening rate was greatly accelerated with the addition of Ga, Al or Zn, and was retarded with the addition of Pd. This tendency can be expected that the addition of Pt reduces the stage I in dental gold alloys as reported in CuAu-xPt alloys by El Araby [16].

It is noted that there is one more very important difference between the groups A and B. It is the atomic ratio of copper and gold, Cu/Au, which is shown in Table 1. The group A, which produces two steps ordering, has nearer equiatomic composition than the group B. Ouchida *et al.* [20] has reported that deviation from stoichiometry produced the retardation of ordering in CuAu alloy. It is considered that the decrease of the atomic ratio Cu/Au yields the retardation of the ordering or the decrease of the stage I as can be seen in Figs. 1 and 2. This modification may be favorable for controlling the mechanical properties in dental casting gold alloys.

It is interesting that the phase transformation behavior in resistivity was simplified by additional elements. The phase transformation in dental gold alloy is based on the formation of CuAu ordered phase. The ordering of binary CuAu alloy progresses in three stages [21]. As mentioned above [16], the ordering progressed in two stages by platinum addition. Addition of silver may also be considered in the phase transformation behaviors. Sakurana [22] has reported the phase transformation in CuAu-14at%Ag-(0–7.5)at%Pt alloys. The resistivity curve in a CuAu-14 at%Ag-6 at%Pt alloy resembles that of the specimen No. 3 in Fig. 1.

5 Conclusions

Age-hardening characteristics during continuous heating in commercial dental gold alloys were investigated by means of electrical resistivity measurements, hardness tests, and X-ray diffraction. Depending on the platinum contents and the atomic ratio of gold and copper in each alloy, two distinguishable behaviors were detected. The phase transformation progresses in two steps (stages I and II). Increase of the platinum addition in gold alloys tends to retard the rate of the reaction and decreases remarkably the amount of stage I.

References

1. E. M. WISE, W. CROWELL and J. T. EASH, *Trans. Met. Soc. AIME* **99** (1932) 363.
2. E. M. WISE and J. T. EASH, *Trans. Met. Soc. AIME* **104** (1933) 276.
3. A. PRASAD, T. ENG and K. MUKHERJEE, *Mater. Sci. Eng.* **24** (1976) 179.
4. K. F. LEINFELDER and D. F. TAYLOR, *J. Dent. Res.* **56** (1977) 335.
5. K. HISATSUNE, M. NAKAGAWA, K. UDOH, B. I. SOSROSOEDIRDJO and M. HASAKA, *J. Mater*, Sci.; *Mater. Med.* **1** (1990) 49.
6. T. TANI, K. UDOH, K. YASUDA, G. VAN TENDELOO and J. VAN LANDUYT, *J. Dent. Res.* **70** (1991) 1350.
7. K. HISATSUNE, Y. TANAKA, K. UDOH, A. M. EL ARABY, K. IWANUMA and K. YASUDA, *Dent. Mater. J.* **12** (1993) 233.
8. K. HISATSUNE, *Jap. J. Met.* **42** (1978) 118.
9. K. HISATSUNE, Y. TANAKA, T. TANI, K. UDOH and K. YASUDA, *J. Mater. Sci.; Mater. Med.* **3** (1992) 54.
10. K. HISATSUNE, K. BABA, M. HASAKA, T. MORIMURA, Y. TANAKA and K. UDOH, *J. Alloys & Comp.* **230** (1995) 94.
11. K. HISATSUNE, Y. TANAKA, K. UDOH and K. YASUDA, *J. Mater. Sci. Mater. Med.* **8** (1997) 177.
12. K. HISATSUNE, A. SAKURANA, K. HAMASAKI, R. HERNANDEZ and J. P. SALONGA, *J. Alloys & Comp.* **261** (1997) 308.
13. A. M. EL ARABY, Y. TANAKA, K. UDOH, K. HISATSUNE and K. YASUDA, *J. Alloys & Comp.* **206** (1994) 217.
14. K. HISATSUNE, M. OHTA, T. SHIRAISHI and M. YAMANE, *J. Dent. Res.* **61** (1982) 805.
15. M. HIRABAYASHI and S. WEISSMANN, *Acta Met.* **10** (1962) 25.
16. A. M. EL ARABY, A Doctoral Dissertation in Nagasaki University. (1994).
17. R. I. HERNANDEZ, K. UDOH, Y. TANAKA, HTAIN WINN, Y. TAKUMA and K. HISATSUNE, *Dent. Mater. J.* **18** (1999) 235.
18. M. OHTA, T. SHIRAISHI, M. NAKAGAWA and S. MATSUYA , *J. Mater. Sci.* **29** (1944) 2083.
19. T. SHIRAISHI and M. OHTA, *J. Mater. Sci.* **24** (1989) 1049.
20. R. OUCHIDA, T. SHIRAISHI, M. NAKAGAWA and M. OHTA, *J. Mater. Sci.* **30** (1995) 3863.
21. K. HISATSUNE, Y. TANAKA, K. UDOH and K. YASUDA, *Intermetallics* **3** (1995) 335.
22. A. SAKRANA, A Doctoral Dissertation in Nagasaki University. (1997).