Effects of indium addition to CuAu alloy on phase transformation behaviors

K. Hisatsune^{*1}, K. Udoh², T. Shiraishi¹,
Y. Takuma¹, E. Miura¹ and T. Fujita¹

¹ Department of Dental and Biomedical Materials Science, Unit of Medical and Dental Sciences, Nagasaki University Graduate School of Biomedical Sciences, Nagasaki 852-8588, Japan

² Institute for Biomedical Research and Education, Yamaguchi University Science Research Center

* Corresponding author; Kunihiro Hisatsune,
E-mail address: hisatsune@nagasaki-u.ac.jp
Tel and Fax: +81-95-819-7656

Abstract

The effects of indium addition to CuAu on the alloy phase transformation behavior were investigated by hardness tests, electrical resistivity measurements, X-ray diffraction and transmission electron microscopy. These established that indium additions lower the critical temperature and stabilize the CuAu II phase at room temperature. Formation of the long period ordered phase produces an age-hardening; although this age-hardening is retarded, the degree of hardening is comparable to that in CuAu. It was noted that the axial ratio increases and the anti-phase domain size decreases.

Keywords: metals and alloys; gold dental alloys; solid state reactions; phase transitions; X-ray diffraction; transmission electron microscopy

1 Introduction

Gold alloys are one of the most popular dental restorative materials. International Standard ISO 1562:2004-05-01 requires that Type 4 gold alloys should be age-hardenable and in these alloys this is achieved by the formation of the CuAu ordered structure [1-6]. Recently, Ohta et al. [7-9] succeeded in initiating hardening at room temperature by additions of gallium to equiatomic CuAu alloy, i.e. natural age-hardening. However, the phase transformation behaviors have not yet been satisfactorily explained. Sato and Toth [10] have reported that an increase of electron-atom ratio by adding a third element to CuAu stabilizes a long period superlattice, CuAuI. Indium was used as an additional element in the present alloys, due to its low melting point and its increase in the electron-atom ratio.

The aim of the present study was to clarify the effects of indium additions on the phase transformation in a CuAu alloy by using electrical resistivity measurements, hardness tests, X-ray diffraction (XRD) and transmission electron microscopy (TEM).

2 Materials and methods

Each alloy was prepared in 100g samples by gas melting in carbon crucible using 99.99wt% Au, Cu and In, which were cold rolled and then annealed at 923°K to homogeneous sheet specimens 0.5mm in thickness. The chemical compositions of four specimens are shown in Table 1. They have the approximate compositions of $\text{Cu}_{0.5}\text{Au}_{0.5-x}\text{In}_x$ ($x=0, 0.02, 0.04$ and 0.06).

The alloys were firstly solution-treated at 723°K for 1.8ks and quenched into iced brine, and were immediately stocked in a refrigerator to prevent any phase transformation. Thereafter, we carried out anisothermal annealing of the samples prior to electrical resistivity and isothermal annealing for hardness tests, XRD and TEM.

Electrical resistivity measurements were made in vacuum by a four-terminal potentiometric method using foil specimens 0.1mm thick, 3mm wide and 25mm long, during a continuous heating at a rate of 1.67×10^{-3} K/s (0.1°C/min). Hardness tests were completed using a diamond pyramid

Table 1

Chemical compositions of the alloys used

Alloys	Chemical composition (at%)		
	Cu	Au	In
CuAu	50.43	49.57	0
CAI-2	49.13	48.83	2.04
CAI-4	49.45	46.58	3.97
CAI-6	49.73	44.44	5.83

hardness indenter with 300g load. Each hardness value quoted is the average of five indentations. The structural changes were examined by XRD and TEM. The XRD study was carried out on filed and appropriately heat-treated powder specimens by using nickel-filtered $\text{CuK}\alpha$ radiation (RAD-rA, Rigaku Corp., Japan). For the TEM study, discs of 3mm diameter were produced, given the appropriate annealing treatment and then electrothinned using a double-jet technique in a solution of 35g CrO_3 , 200mL of CH_3COOH and 10mL of H_2O . The TEM observations were completed at 200kV (H-800, Hitachi Co., Tokyo, Japan).

3 Results and discussion

3.1 Electrical resistivity changes during anisothermal annealing

Fig.1 shows anisothermal annealing curves of electrical resistivity at a heating rate of 1.67×10^{-3} K/s in the four specimens after the solution treatment and then quenching. Normalized resistivity (ρ_T/ρ_{723}) is a ratio of the resistivity at each measured temperature (T) and to that at the solution-treated temperature (723°K). In the case of equiatomic CuAu alloy, the variation has been already reported [11]. The ordering to CuAu I proceeds in three stages (stages I, II and III). However, indium additions produce remarkable variations, particularly the retardation of the reaction. In fact two modifications were confirmed with increasing In content. The first is a big decrease in amount of the resistivity change, because of the reduction in the degree of the order in ternary ordered state compared to binary ordered structure, CuAu. The second modification is a lowering of the critical temperature in order-disorder transformation as can be seen by arrows in Fig.1.

3.2 Isothermal annealing behaviors

3.2.1 Hardening behaviors

Hardness tests were performed on four specimens (CuAu, CAI-2, CAI-4 and CAI-6), annealed at room temperature, 373°K, 423°K, 473°K and 523°K for various times. As similar behavior was observed in the four specimens, only the data of CAI-4 is shown, Fig.2. General hardening behaviors were observed. At 473°K and 523°K, the hardening commences quickly. However, ageing at 373°K and 423°K produces a gradual hardening. At room temperature, only very slow reaction occurs. In order to compare the effects of indium additions, the age-hardening curves of four specimens aged at 423°K are shown in Fig.3. Indium additions produce a retardation of age-hardening as deduced from the resistivity change, and a decrease of maximum hardness.

3.2.2. Crystal structural changes

It was confirmed that three alloys (CAI-2, CAI-4 and CAI-6) produced similar behavior in XRD studies as in the hardness tests. Therefore, the data of CAI-4 alloy aged at 423°K is used

Figure 1

Variations of anisothermal annealing curve with electrical resistivity at a heating rate of 1.67×10^{-3} K/s in CuAu-In alloys after the solution treatment and then quenching

Figure 2

Age-hardening curves in CAI-4 aged at room temperature, 373°K, 423°K, 473°K and 523°K

as a representative sample of these alloys. Fig.4 shows the variation of XRD profile on the higher angle side in CAI-4 aged at 423°K for various times. Two sharp reflections with doublet, 331 and 420, correspond to those from a disordered phase with face-centered cubic (fcc) lattice. With increasing aging time, the reflections become broad and decrease in intensity. Severe broad peaks are confirmed at ageing for 300ks and could indicate reasonable hardening as seen in Fig.3. By aging for 1Ms, the disordered phase completely

Figure 3

Age-hardening curves in CuAu, CAI-2, CAI-4 and CAI-6 aged at 423°K

Figure 5

Variation of lattice parameter in CAI-4 aged at 423°K

Figure 4

Variation of XRD profile on higher angle side in CAI-4 aged at 423°K

Figure 6

Variation of XRD profile in the vicinity of the fundamental reflections, 111 and 200 in CAI-4 aged at 423°K

disappears and a new phase appears. Fig.5 shows the variation of the lattice parameter with ageing time in CAI-4 aged at 423°K. The lattice parameter was precisely measured using an extrapolative function of Nelson-Riley [12]. The lattice parameter gradually decreases with increasing ageing time and the extent of the variation is in good agreement with that of the hardness as shown in Fig.3. Small decreases in the lattice parameter suggests that some precipitation occurs in the grain interior as noted by Krawitz and Sinclair

[13]. Fig.6 shows the variation of XRD profile in the vicinity of the fundamental reflections, 111 and 200, in CAI-4 aged at 423°K. At 30ks ageing, the base of the 200 line becomes broad. With increasing the ageing time, a variation is detected, and the coexistence of the disordered and new phases can be confirmed. The coexistence continues to 600ks ageing; ageing for 3Ms produces only the new single phase which is identified as CuAu II with $L1_{0-s}$ structure. Fig.7 shows variation of the superlattice reflections of CuAu II, 011,

Figure 7

Variation of the superlattice reflections of CuAu II, 011, 190 and 1110 in CAI-4 aged at 423°K

190 and 1110, in CAI-4 aged at 423°K. With increasing ageing time, the reflection lines become sharp and stronger in intensity indicating that the degree of order and/or the volume fraction increases. Indium additions to the CuAu alloy stabilizes the CuAu II phase, and the CuAu I phase disappears or moves to the lower temperature region.

Fig.8 shows (a) the selected-area electron diffraction pattern with 001 zone, (b) 001_x and (c) 001_y dark field (DF) images in the CAI-4 aged at 523°K for 1ks, that correspond to the hardness peak. Following Ogawa and Watanabe [14], split reflection characteristics of the long-period antiphase domain boundary (LPAPB) structure from the CuAu II ordered phase can be recognized. The DF images in Figs.8 (b) and (c) exhibit the x- and y-variant respectively of ordered platelets. In these micrographs, it can be observed that the LPAPBs of the CuAu II orthorhombic phase are formed as parallel block thin stripes in twin platelets. Fig.9 shows variations of the axial ratio, a/c and the antiphase domain size, M , with indium content in the specimens aged at 523°K for 1ks and at 473°K for 30Ms, that correspond to the hardness peak and the equilibrium state respectively. With increasing indium content, the axial ratio increases and the antiphase domain size decreases. If we can consider the stability of tetragonality by the axial ratio and the antiphase domain size, the variations indicate a closeness to the cubic, and suggests more random regularity. This confirms a decrease in resistivity change as stated above, and with indium occupation on both sites as reported previously elsewhere [15].

Figure 8

DF images and SAD pattern of the CAI-4 alloy aged at 523K for 1ks. (a) SAD pattern of [001], DF images of (b) 001_x and (c) 001_y

Figure 9

Variations of the axial ratio and the antiphase domain size with indium content in the CuAu alloy aged at 523°K for 1ks and at 473°K for 30Ms

4 Conclusions

The effects of indium additions on the phase transformation behaviors of CuAu alloy have been examined by hardness tests, electrical resistivity measurements, XRD and TEM. The main results are as follows;

1. Indium addition lowers the critical temperature and holds CuAu II phase at room temperature.
2. The formation of long period ordered phase produces the age-hardening.
3. Though the age-hardening is retarded by indium addition, degree of the hardening is as same as that in CuAu.
4. Indium addition increases the axial ratio and decreases the antiphase domain size in ternary alloy.

About the authors

Kunihiro Hisatsune is professor and chairman of Department of Dental and Biomedical Materials Science, Ph.D. in 1979, **Koichi Udoh** is associate professor of Institute for Biomedical Research and Education, Ph.D. in 2000, **Takanobu Shiraishi** is associate professor of Department of Dental and Biomedical Materials Science, Ph.D. in 1984, **Yasuko Takuma** is research associate of Department of Dental and Biomedical Materials Science, **Eri Miura** is assistant professor of Department of Dental and Biomedical Materials Science, Ph.D. in 1999 and **Takeshi Fujita** is assistant professor of Department of Dental and Biomedical Materials Science.

References

- 1 K.F. Leinfelder, W.J. O'Brien, D.F. Taylor, *J. Dent. Res.*, 1972, **51**, 900
- 2 A. Prasad, T. Eng, K. Mukherjee, *Mater. Sci. Eng.*, 1976, **24**, 179
- 3 K. Yasuda, M. Ohta, *J. Less-Comm. Met.*, 1980, **70**, P75
- 4 K. Hisatsune, M. Nakagawa, K. Udoh, B.I. Sosrosoedirdjo, M. Hasaka, *J. Mater. Sci.; Mater. Med.*, 1990, **1**, 49
- 5 K. Hisatsune, K. Udoh, M. Nakagawa, M. Hasaka, *J. Less-Comm. Met.*, 1990, **160**, 247
- 6 T. Tani, K. Udoh, K. Yasada, G. Van Tendeloo, J. Van Landuyt, *J. Dent. Res.*, 1991, **70**, 1350
- 7 M. Ohta, T. Shiraishi, M. Nakagawa, S. Matsuya, *J. Mater. Sci.*, 1994, **29**, 2083
- 8 R. Ouchida, T. Shiraishi, M. Nakagawa, M. Ohta, *J. Mater. Sci.*, 1995, **30**, 3863
- 9 M. Ohta, T. Shiraishi, R. Ouchida, M. Nakagawa S. Matsuya, *J. Alloys & Comp.*, 1998, **265**, 240
- 10 H. Sato, R.S. Toth, *Phys. Rev.*, 1961, **124**, 1833
- 11 K. Hisatsune, Y. Tanaka, K. Udoh, K. Yasuda, *Intermetallics*, 1995, **3**, 335
- 12 J.B. Nelson, D.P. Riley, *Proc. Phys. Soc., London*, 1945, **57**, 160
- 13 A. Krawitz, R. Sinclair, *Phil. Mag.*, 1975, **31**, 697
- 14 S. Ogawa, D. Watanabe, *Phys. Soc. Japan*, 1954, **9**, 475
- 15 K. Hisatsune, T. Shiraishi, Y. Takuma, E. Miura and T. Fujita, *Dent. Mater. J.*, 2008, To be published