Age-hardening Mechanism of Equiatomic AuCu and AuCu-Ag Pseudo-binary Alloys

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AuCu-Ag pseudo-binary phase diagram was illustrated and the difference in age-hardening mechanism with changes of silver content in the AuCu-Ag pseudo-binary system was studied. In the equiatomic AuCu and low silver alloy, age-hardening was due to the formation of the AuCu I type ordered domains. Growth of the domains caused twinning which resulted in remarkable softening of the alloy. On the other hand, age-hardening in the high silver alloy was attributed to the dual mechanisms of two phase separation and ordering which was initiated by spinodal decomposition.

Key Words: Gold alloy, Age-hardening, Electron microscopy

INTRODUCTION

Principal constituents of the dental gold alloys are gold, copper and silver. Since the ternary system of the gold-copper-silver is characterized by ordering in the gold-copper system and by two phase decomposition in the copper-silver system, age-hardening mechanism varies greatly depending on the composition of the alloy.

The purpose of the present study is to clarify the age-hardening mechanism of the gold-copper-silver ternary alloys as a function of the composition. Little work has been reported on the systematic study of age-hardening mechanism of this ternary system. The authors¹⁾ have studied the difference in age-hardening mechanism with changes of gold content in this system, in which the atomic ratio of copper to silver remained at 76 to 24. The results indicated that age-hardening was due to the formation of the AuCu I type ordered phase in the high gold content alloy (18K) and to the formation of the AuCu II type ordered phase in the low gold content alloys (16K and 14K). Contribution of the precipitation to the hardening became significant with decrease in the gold content.

In this study, difference in age-hardening mechanism with changes of silver content in the gold-copper-silver ternary system was studied. For this purpose, AuCu-Ag pseudo-binary phase diagram was firstly determined from the electrical resistivity curves and electron diffraction patterns. Secondly, age-hardening characteristics of equiatomic AuCu and AuCu-Ag pseudo-binary alloys were examined by means of hardness tests, X-ray and electron diffraction and transmission electron microscopy.

MATERIALS AND METHODS

Chemical compositions of the specimens employed are listed in Table 1. They were prepared by melting 99.99% Au, Cu and Ag in vacuo in a high frequency induction furnace.

Table 1 Chemical composition of specimens used (at%)

Specimen	Au	Cu	Ag
No. 1	50.6	49.4	0
No. 2	46.9	47.5	5.6
No. 4	36.2	41.4	22.4
No. 6	33.4	35.5	31.1

After homogenizing the ingots at 800°C for 50 hr, billets of $2 \times 2 \times 20$ mm³ and sheets of 0.1 mm thick were obtained by alternate swaging and annealing of the ingots. They were solution treated at 500°C (specimens No. 1 and No. 2) and 700°C (specimens No. 4 and No. 6) for 1 hr followed by iced-brine quenching.

Hardness tests were made using a diamond pyramid hardness indenter with a 500 g load. The Vickers hardness was obtained as the average of five indentations.

Electrical resistivity was measured during continuous heating at a heating rate of 0.1°C/min from room temperature to the solution treated temperature.

X-ray diffraction study was carried out on the filed and appropriate heat treated powder specimens using Ni filtered CuK_α radiation.

Three mm dia discs were punched out of the heat treated sheet specimens. They were electrothinned to transparency by a double-jet technique in a solution of 35 g of CrO_3 , 200 ml of CH_3COOH and 10 ml of distilled water. Electron microscope used was a JEM-1000 (HVEM Lab. Kyushu Univ.) operating at 1000 kV.

RESULTS

(1) AuCu-Ag pseudo-binary phase diagram

Figure 1 exhibits the changes in electrical resistivity of specimens during continuous heating. Each curve was normalized by setting the value at 700°C to unity. In case of specimens No. 1 and No. 2, no phase transformation is expected to occur above 500°C, and

Figure 1 Changes of electrical resistivity during continuous heating

Figure 2 AuCu-Ag pseudo-binary phase diagram. The broken line shows the expected spinodal curve

resistivity-temperature curves exhibited straight line above 411 °C (No. 1) and 368 °C (No. 2). Therefore values of No. 1 and No. 2 at 700 °C were obtained by extrapolating the straight lines to 700 °C. On heating the disordered solid solution, resistivity decreased through two stages. After showing the minimum value, resistivity increased through several stages with some kinks on the curve. Because of slow heating rate (0.1 °C/min), changes in the increasing stage are thought to correspond to the changes following equilibrium state at each temperature. Consequently it is reasonable to consider that kink temperatures correspond to the temperatures at which phase transformations occur.

Figure 2 shows the AuCu-Ag pseudo-binary phase diagram which is illustrated by plotting the kink temperatures against silver content. The reliability of this diagram was confirmed by determining the co-existing phases in each regions in the diagram by electron diffraction method.

(2) Isothermal age-hardening curves

Phase diagram of Figure 2 is helpful in predicting the phase transformations which are expected to be responsible for age-hardening. By aging specimens No. 1 and No. 2 at 300 °C, ordering of disordered solid solution (face centered cubic, fcc) to the AuCu I type (face centered tetragonal, fct) may occur. Ordering to the AuCu II type (orthorhombic) is expected to occur by aging specimens No. 1 and No. 2 at the temperature just below the critical temperature. On the other hand, aging of specimens No. 4 and No. 6 at 300 °C may cause the phase separation of α into the Ag-rich α_2 solid solution and the AuCu II type ordered phase.

Figure 3 represents the isothermal age-hardening curves of specimens aged at 300 °C. All specimens exhibit rapid hardening by 30 sec aging. This rapid hardening is followed by gradual softening on specimen No. 1. Softening also appears on specimen No. 2 after 50 min. On the other hand, hardness of specimens No. 4 and No. 6 increase gradually after rapid hardening.

(3) X-ray diffraction

Figure 4 shows the changes in the ordering parameter S' and axial ratio c/a of the AuCu I type tetragonal structure with aging time at 300 °C. Parameter S' is proportional to the degree of order S , and S' at time t was calculated by the following equation,

Figure 3 Isothermal age-hardening curves at 300 °C

Figure 4 Changes in the ordering parameter S' and axial ratio c/a of specimens No. 1 and No. 2 aged at 300 °C

$$S' = (\sqrt{I_s/I_f})_t / (\sqrt{I_s/I_f})_{eq}$$

where I_s and I_f are integrated intensity of super and fundamental line, respectively. Value of $\sqrt{I_s/I_f}$ at 5000 min was employed as the equilibrium value $(\sqrt{I_s/I_f})_{eq}$ at 300°C.

It is shown in Figure 4 that curves of S' and c/a are both shifted to the long aging time side by the addition of 5.6 at% Ag, that is, addition of Ag suppresses the ordering of the AuCu.

Spinodal in the Au-Cu-Ag system was calculated by Yamauchi et al.²⁾. According to their results, specimens No. 4 and No. 6 are expected to spinodally decompose. Figure 5 shows the change in the intensity profile of the X-ray diffraction peak of specimen No. 6 at 300°C with aging time. Side-bands appeared in the vicinity of the main peak. They approached the main peak with aging time, accompanying an increase in their intensity. Variation of wavelength of the modulation with aging time was calculated using Daniel-Lipson's equation³⁾ and is shown in Figure 6 with the variation of hardness. Wavelength was found to increase proportionally with the cube root of aging time from 5 to 40 min.

(4) Electron microscopic observations

Figure 7(a) is a 001 dark field image of specimen No. 1 aged at 300°C for 1 min which corresponds to the hardness peak. The AuCu I type ordered domains are observed to form along [110] and $[\bar{1}10]$ direction of the matrix. Streaks along $\langle 110 \rangle$ and $\langle 100 \rangle$ are recognized in the selected area diffraction pattern (Figure 7(b)). Analogous features were observed on specimen No. 2 aged at 300°C for 50 min which corresponded to its hardness peak.

Figure 8(a) and (b) are bright field images taken from specimen No. 1 aged at 300°C for 5 min (a) and 100 min (b) which correspond to the overaged state. These structures are characterized by twin.

Figure 9 is a bright field image taken from specimen No. 6 aged at 300°C for 30 min.

Figure 5 Side-bands of X-ray diffraction peak in specimen No. 6 aged at 300°C

Figure 6 Variations of wavelength of modulation ($\bar{\lambda}$: solid circle) and hardness (H_v : open circle) with aging time in specimen No. 6. EM indicates $\bar{\lambda}$ measured by transmission electron microscopy

Figure 7 001 dark field image (a) and selected area diffraction pattern (b) of specimen No. 1 aged at 300°C for 1 min

Figure 8 Bright field images of specimen No. 1 aged at 300°C for 5 min (a) and 100 min (b)

Figure 9 Bright field image of specimen No. 6 aged at 300°C for 30 min

A modulated structure parallel to the $[010]$ direction of the matrix is seen. Observed wavelength of the modulation was in good agreement with that calculated from the X-ray diffraction data (Figure 6).

Figure 10(a) is a bright field image taken from specimen No. 6 aged at 300°C for 30000 min, and (b) is corresponding diffraction pattern. The structure in Figure 10(a) is characterized by block-like structure, not by twinned structure. It consists of alternating AuCu II type ordered phase and the Ag-rich α_2 phase, as indicated in the diffraction pattern.

Figure 10 Bright field image of specimen No. 6 aged at 300°C for 30000 min (a) and corresponding diffraction pattern (b)

DISCUSSION

Transmission electron microscopy revealed that the hardening in specimens No. 1 and No. 2 were attributed to the formation of the AuCu I type ordered phase which accompanied elastic strain field, and that the softening corresponded to the twinning in the ordered phase which relieved the strain.

Ordering in the equiatomic AuCu alloy is believed to initiate with the nucleation of ordered domain on $\{110\}$ plane of the matrix fcc^{(4), (5), (6)}. Line up of ordered domains along $\langle 110 \rangle$ direction in Figure 7 seems to indicate that the habit plane of the ordering in the AuCu I is $\{110\}$. But the results of studies on the aging of Cu-2%Be^{(7), (8)} and Ag-Pd-Cu-Au alloys^{(9), (10), (11)} suggest that the $L1_0$ type (AuCu I type) structure is formed along (001) plane of the matrix fcc. In these alloys, G.P. zone of one atomic layer is formed on every two layers of (002) plane, which yields tetragonal structure and $\langle 100 \rangle$ streaks on the diffraction spots.

Computer simulation study on a distribution of tetragonal precipitates in a cubic crystal⁽¹²⁾ indicates that like-variant particle align along $\{110\}$ plane to minimize the elastic strain energy. $\langle 110 \rangle$ configuration of domains causes $\langle 110 \rangle$ relrods in the diffraction pattern.

Considering the above facts, ordering in the AuCu is assumed to start by the nucleation on (001) plane of the matrix which aligns along $\langle 110 \rangle$ to minimize the elastic strain. Such mechanism is strongly supported by "tweed structure" shown in Figure 7(a) and $\langle 110 \rangle$ and $\langle 100 \rangle$ relrods in the diffraction pattern in (b). Further works on the habit plane of the AuCu ordering is now in progress and will be described elsewhere.

Growth of the ordered domain on (001) plane results in twinning along (101). Hansson and Barnes⁽¹³⁾ suggested that twin in the AuCu I is generated by the movement of $\frac{1}{2}[101]$ dislocations on successive (101) planes. $\frac{1}{2}[101]$ Burgers vector is parallel to the maximum shear strain field caused by the tetragonality⁽⁷⁾. $\langle 110 \rangle$ relrods in the diffraction pattern is an indication of such a situation. By twinning, elastic strain will be relieved and apparent softening occurs.

Specimens No. 1 and No. 2 show rapid hardening by 30 sec aging. Such a rapid reaction is attributed to the nucleation of ordered domains which is achieved by the consumption of quenched-in excess vacancies. However the time at which hardness peak

appear is remarkably delayed in specimen No. 2. Morphology of specimen No. 2 at the hardness peak was analogous to that of specimen No. 1 and no twin was observed. These facts indicate that the time at which twinning starts is delayed by the addition of silver.

Twinning is considered to occur when the size of ordered domain become larger than the critical twin nucleus size⁶⁾. The critical twin size will be larger in the specimen No. 2 than that in the specimen No. 1, because of larger axial ratio (Figure 4).

High silver alloys No. 4 and No. 6 exhibited modulated structure. They developed into block-like structures which consisted of alternating AuCu II type ordered phase and the Ag-rich α_2 phase.

Figure 6 shows that wavelength of the modulation is almost constant until 5 min aging and that most of the hardening is attained in this period. Accordingly, it is presumed that the amplitude of the concentration fluctuation increases during this period and the resulting strain field causes rapid hardening of the alloy.

Prolonged aging forms a block-like structure parallel to the modulation. Usually, coarsening of the structure leads to the softening. But the ordering in the Cu-rich phase proceeds and, as shown in Figure 3, hardness increases gradually.

CONCLUSIONS

AuCu-Ag pseudo-binary phase diagram was illustrated and age-hardening mechanism of the equiatomic AuCu and AuCu-Ag pseudo-binary alloys were studied by means of hardness test, X-ray diffraction and transmission electron microscopy.

Principal results obtained are as follows;

- (1) Age-hardening mechanism of the equiatomic AuCu alloy and AuCu-5.6at%Ag alloy at 300°C was the formation of the AuCu I type ordered phase which was coherent with the matrix.
- (2) The AuCu I type ordered domains were formed along $\langle 110 \rangle$ direction of the matrix which accompanied elastic strain field. Growth of the domains caused twinning which resulted in the softening of the alloy by releasing elastic strain.
- (3) Twinning of the ordered phase was suppressed by the addition of silver.
- (4) Age-hardening of high silver content alloy was attributed to the dual mechanisms of phase separation and ordering.
- (5) Phase separation was thought to proceed by the spinodal decomposition, formation of modulated structure, increase in the wavelength and growth into a block-like structure which consisted of alternating AuCu II type ordered phase and the Ag-rich α_2 phase. Most of the hardening was attained in the initial stage of aging by the formation of modulation. Successive aging increased hardness by the ordering in the Cu-rich phase.

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本号掲載論文の和文抄録

床用レジンへの金めっき条件について

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床用レジン表面の性状を向上させるために金めっき条件並びに耐磨耗性と耐変色性について検討した。

ハルセル試験装置によって、全電流 1, 2 A, めっき時間 5, 10, 20 分の各条件下で金めっきを行い、適性電流密度と均一電着性を測定した。次に 200 g 荷重の歯ブラシで磨耗試験を行い、精度 1/1000 g の上皿電子天秤によって磨耗量を測定した。さらに 5 種類の義歯洗浄剤に浸漬し、変色試験を行った。

その結果、めっき時間 5 分では金めっきは不良であった。適性電流密度は 1 A で 1.8 A/dm^2 以下であり、2 A で 2.6 A/dm^2 以下であった。均一電着性は 1 A, 10 分で 48.1%, 1 A, 20 分で 56.5%, 2 A, 10 分で 49.0%, 2 A, 20 分で 31.1% であった。10 万回の磨耗試験では磨耗量の検出は不可能であった。義歯洗浄剤によって変色したのもあったが、表面を清掃することによって、容易に除去できた。

等原子比 AuCu および AuCu-Ag 凝二元合金の時効硬化機構

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AuCu-Ag 凝二元状態図を決定し、AuCu-Ag 凝二元合金の時効硬化機構の Ag 含有量変化による相違をしらべた。等原子比 AuCu 合金および低 Ag 濃度合金では AuCu I 型規則化ドメインの形成が硬化の原因であった。ドメインの成長によって双晶化が生じ、合金は軟化した。一方、高 Ag 濃度合金においては時効初期にスピ

ノーダル分解によって変調構造が形成され、急速な硬化を示した。その後の時効によって、変調構造に平行でしか Ag-rich 相と Cu-rich 相とが交互に配列するブロック状組織となったが、Cu-rich 相中での規則化 (AuCu II 型) が進行するために、合金は徐々に硬化した。

各種アマルガムの硬さの経時的変化

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入手可能な各種アマルガムアロイの硬化途上での硬さの変化を練和開始 1 時間後から 30 日後まで経時的に測定した。マイクロビッカース硬度計を用い 37℃ の環境下で測定したところ、硬さの発現と増加にはアロイの粒状や組成によって特徴があることがわかった。すなわち、粒状からいえば球状アロイが、組成からいえば高銅型アロ

イがそれぞれ削片状アロイ、従来型アロイに比べて、より短時間で硬さが大きくなり最大に達した。高銅型アロイのうちでも単一組成型アロイは硬さの発現が特に短時間で起こるものが多く、1 時間硬さは 24 時間硬さの約 60% に達した。30 日硬さは 24 時間硬さに類似していたので、このタイプのアロイは他のものに比べて硬化がより