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Low temperature ageing in equiatomic CuAu and Cu–Au–Pd ternary alloys

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Low temperature ageing at 37° C in an equiatomic CuAu alloy and several Cu–Au–Pd ternary alloys in the CuAu–$Cu_{0.6}Pd_{0.4}$ pseudobinary system was studied. Age-hardening and a decrease in electrical resistivity were observed in the CuAu alloy and Cu–Au–Pd ternary alloys containing palladium up to 11 at. %. These phenomena were caused by the progress of long-range ordering in the CuAu I type superstructure with the aid of quenched-in excess vacancies. The rate of low temperature ageing decreased with increasing palladium concentration. This was presumed to be due to the increase in migration energy of a quenched-in vacancy with the palladium concentration.

1. Introduction

The Cu–Au–Pd ternary system forms a single phase region with CuAu I type superstructure over the wide range of composition [1]. This single phase region extends from CuAu toward $Cu_{0.6}Pd_{0.4}$. Recently the authors reported that the mechanical properties of alloys possessing compositions in this region could be markedly improved by the appropriate heat treatment [2]. Corrosion resistance of these alloys was proved to be sufficient for dental use [3].

To obtain sufficient strength for various purposes, dental alloys have been subjected to the age-hardening treatment at high temperatures. However, if dental alloys possess the age-hardenability at the oral environmental temperature, it becomes unnecessary for alloys to be subjected to age-hardening treatment at high temperatures. Low temperature ageing phenomena in alloys is known to occur mainly in aluminium-based alloys.

The authors previously observed that the electrical resistivity of an equiatomic CuAu alloy began to decrease gradually from around 30° C when this alloy was quenched into ice brine from above the order–disorder transition temperature (T_c) and continuously heated from room temperature at a heating rate of $0.1° C\,min^{-1}$ [4]. This behaviour suggests that the ordering reaction of this alloy may occur at the oral environmental temperature (37° C). In addition to this fact, the ordering reaction of CuAu I type superstructure in the above mentioned Cu–Au–Pd single-phase alloys containing palladium less than about 13 at. % was found to progress very rapidly [5]. This finding also implies that the low temperature ageing possibly occurs in these alloys.

In this study, low temperature ageing characteristics of an equiatomic CuAu alloy and several Cu–Au–Pd ternary alloys possessing compositions in the single-phase region with CuAu I type superstructure were examined at 37° C. The mechanism of the low temperature ageing reaction and effect of palladium addition on the rate of low temperature ageing were discussed.

2. Materials and methods

Chemical compositions of alloys examined are listed in Table I. Fig. 1 is a part of the isothermal section of Cu–Au–Pd ternary phase diagram at 350° C by Raub and Wörwag [1]. Compositions of the experimental alloys are also indicated by the symbols. All of them are noted to exist in the CuAu I type single-phase region.

The specimens were prepared from copper, gold of 99.99% purity and palladium of 99.95% purity. They were accurately weighed to obtain 5 g specimens and were melted in a high-frequency induction furnace and cast to obtain two parallelepiped ingots ($4 \times 4.5 \times 8\,mm^3$). The melting was performed in an argon atmosphere to prevent oxidation of molten metal. Ingots obtained were subjectd to alternate hammering at room temperature and homogenizing treatment at 800° C. The homogenized parallelepiped specimens ($2 \times 6 \times 10\,mm^3$) were finally obtained.

These specimens were solution-treated at 800° C for 1 h followed by direct quenching into ice brine and then aged in a drying oven of which temperature was regulated at 37° C.

A hardness test was carried out by using a micro-Vickers hardness tester with a load of 5 N. The average hardness number and standard deviation were obtained from five indentations.

Electrical resistivity measurements were made by a four-terminal potentiometric method with a direct current of 800 mA. A couple of nickel wires of 0.3 mm in diameter were spot welded at both ends of the solution-treated specimen as current lead wires. Specimens were then dipped in a silicone oil bath regulated at 37° C and subjected to continuous measurements of resistivity.

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TABLE I Chemical compositions of alloys used

Alloy	Composition (at. %)		
	Cu	Au	Pd
CuAu	50.0	50.0	0
H	51.0	44.0	5.0
I	52.0	37.0	11.0
F	54.8	23.9	21.3

Sheet specimens of 70 μm thick were prepared by cold rolling the parallelepiped specimens. These sheet specimens were appropriately heat-treated and electrolytically thinned by a double-jet polishing technique in a solution of 35 g CrO_3, 200 ml CH_3COOH and 10 ml H_2O. Transmission electron microscopic observations were performed by using a JEM-1000 (HVEM Laboratory, Kyushu University) operated at 1 MV.

3. Results

3.1. Age-hardening behaviour

Fig. 2 shows age-hardening curves of specimens aged at 37° C. These specimens were directly quenched into ice brine from 800° C prior to the ageing treatment. The hardness of specimens of CuAu, H and I increased with ageing time. The amount of increase in hardeness was the largest of all in the CuAu specimen. Age-hardening almost stopped after a passage of specific ageing time for each specimen. The age-hardening rate obviously decreased with an increase in palladium concentration. Especially in specimen F, age-hardening did not occur at all.

3.2. The effect of cooling rate of specimen on the age-hardening behaviour

Fig. 3 shows the effect of cooling rate of the CuAu specimen on its age-hardening behaviour at 37° C. The quenching temperature was fixed at 800° C for every specimen. Both the age-hardening rate and the amount of increase in hardness were greatest in the specimen quenched into $-20°$ C ice brine. As regards the air-cooled specimen, an extreme hardening occurred during the air-cooling and no age-hardening was observed at 37° C. The age-hardening rate of the specimen quenched into $-5°$ C silicone oil was very slow.

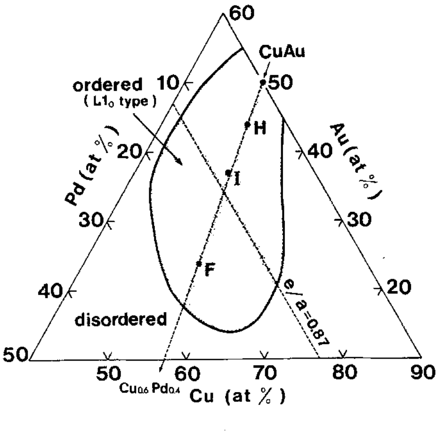

Figure 1 Part of Cu-Au-Pd isothermal section at 350° C and compositions of alloys studied. The shaded area shows the single phase region with CuAu I type ($L1_0$) superstructure.

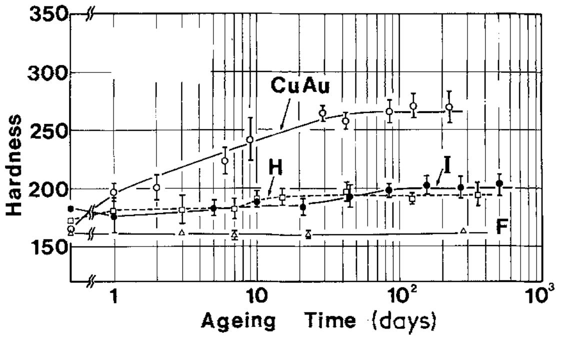

Figure 2 Age-hardening curves of specimens aged at 37° C, T_q = 800° C.

3.3. Changes in electrical resistivity

Fig. 4 shows relative changes in electrical resistivity of specimens CuAu and H aged at 37° C. Each specimen was directly quenched into ice brine from 800° C and then immediately subjected to ageing treatment at 37° C. Electrical resistivity value at ageing time t was normalized by setting that at ageing time zero to unity. The resistivities of both specimens decreased monotonously with time. However, decreasing rates gradually diminished and at last the decrease essentially stopped after the passage of proper ageing time. This feature essentially agrees with the age-hardening behaviour shown in Fig. 2.

3.4. Transmission electron microscopic observations

Fig. 5a is an electron diffraction pattern of the CuAu specimen directly quenched into ice brine from above T_c. Superlattice reflections generated by the CuAu I type superstructure are visible at the positions indicated by arrows. Fig. 5b is a dark-field image obtained from a 001 superlattice reflection encircled in Fig. 5a. Numerous white dots, each of which corresponds to the ordered domain, can be seen in whole crystal grains. These facts indicate that the ordering rate of the CuAu alloy was fast enough to form the ordered CuAu I type fine domains even while the direct quenching into ice brine from above T_c. However, degree of long-range-order in the specimen is supposed to be rather low, because the superlattice reflections in Fig. 5a are faint.

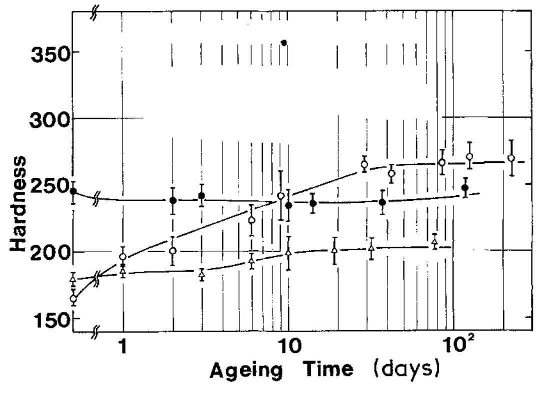

Figure 3 Effect of cooling rate of specimen CuAu on the age-hardening behaviour at 37° C (T_q = 800° C) (○ $-20°$ C ice brine quenched, △ $-5°$ C silicone oil quenched, ● air cooled).

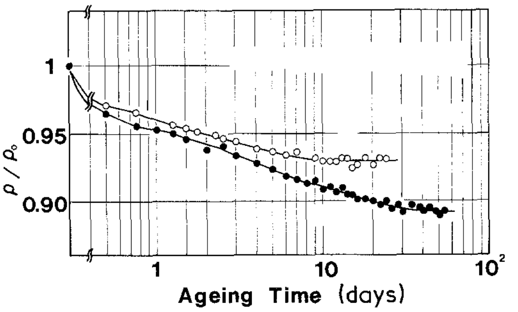

Figure 4 Relative changes in electrical resistivity of specimens CuAu (●) and H (○) aged at 37° C (T_q = 800° C).

4. Discussion

Previous studies on the ordering process of an equiatomic CuAu alloy, performed at relatively high temperatures, made it clear that an increase in hardness [6, 7] and decrease in electrical resistivity [8, 9] occurred with the progress of long-range ordering in CuAu I type superstructure. Accordingly, the experimental results that age-hardening and decrease in electrical resistivity observed in specimens CuAu, H and I at 37° C indicate that long-range-ordering in CuAu I type superstructure also progresses in these alloys even at 37° C.

From the transmission electron microscopy, Hirabayashi and Weissmann [10] proposed the order hardening mechanism of CuAu I. According to their results, the order hardening of CuAu I is caused by coherency strain formed at the interface of ordered domain and surrounding matrix. In fact, weak relrods along ⟨1 1 0⟩ directions are visible around normal spots in the electron diffraction pattern shown in Fig. 5a, indicating the presence of coherency strain. It is, therefore, presumed that low temperature ageing found in this study results from an increase in coherency strain with the progress of long-range ordering in CuAu I type ordered domains.

In general, the low temperature ageing reaction is well known to occur with the aid of quenched-in excess vacancies. As evidenced in Fig. 3, the rate of age-hardening of the specimen CuAu at 37° C accelerated with increase in the cooling rate of the specimen. As the concentration of quenched-in vacancies introduced to the specimen by quenching from high temperatures usually increases with an increase in the cooling rate of the specimen when the quenching temperature is fixed, the above experimental results prove the contribution of quenched-in vacancies to the ageing reaction of CuAu at 37° C. The facts that changes in hardness and in electrical resistivity essentially stopped after the passages of proper ageing time mean that most of the quenched-in vacancies disappeared by those ageing times. Consequently, it is concluded that the low temperature ageing of specimens CuAu, H and I observed at 37° C is caused by the progress of long-range-ordering in CuAu I type superstructure and that such reaction occurs with the aid of migration of quenched-in vacancies.

Low temperature ageing reaction found in this study was obviously suppressed by the addition of palladium to CuAu. The significant factors affecting the rate of low temperature ageing are supposed to be the nucleation rate of ordered domains and diffusion rate of quenched-in vacancies. Therefore these factors are to be discussed below to clarify the effect of palladium addition on the rate of low temperature ageing.

As regards the CuAu–$Cu_{0.6}Pd_{0.4}$ pseudo-binary system, the authors previously reported that the fine ordered domains with CuAu I type superstructure rapidly formed during quenching into ice brine from above T_c in alloys with electron–atom ratio (e/a) was larger than 0.87, while they did not form in alloys with e/a was smaller than 0.87 [5]. This leads to that the fine domains with CuAu I type superstructure are present in the as-quenched specimens H (e/a = 0.95) and I (e/a = 0.89) as well as in the CuAu specimen, while they are not present in the as-quenched specimen F (e/a = 0.79). As shown in Fig. 2, the age-hardening at 37° C occurred in specimens CuAu, H and I, but did not occur in specimen F. This finding agrees well with whether the fine domains with CuAu I type superstructure are present or not in the as-quenched state. The above fact implies that the presence of ordered domains in the as-quenched state is necessary for the low temperature ageing to occur.

It is difficult to estimate precisely the diffusion rate of quenched-in vacancies at 37° C in the alloys examined here. However, variation of diffusion rate of quenched-in vacancies against composition can be derived qualitatively from the activation energies for diffusion at high temperatures. Tournon and Kuczynski [11] reported the activation energy for

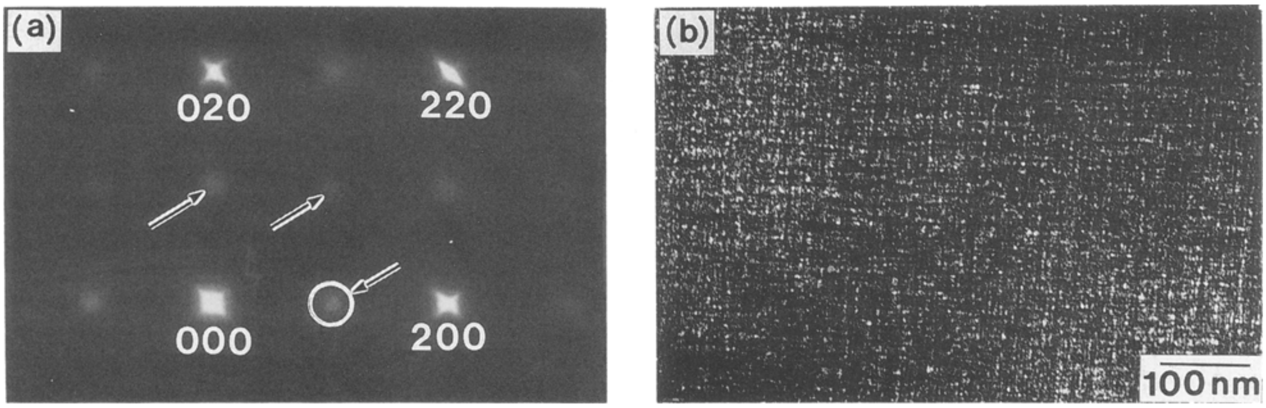

Figure 5 (a) Electron diffraction pattern of CuAu specimen directly quenched into ice brine from above T_c and (b) dark-field image obtained from a 001 superlattice reflection encircled in (a).

diffusion at high temperatures (E) in a Cu–50 at. % Au alloy to be 163 kJ mol^{-1}. Variation of E values in the CuAu–$Cu_{0.6}Pd_{0.4}$ pseudo-binary system has not yet been reported. However, the activation energy for diffusion of palladium in copper is known to be 227 kJ mol^{-1} [12]. This value is considerably higher than the E value in a Cu–50 at. % Au alloy reported by Tournon and Kuczynski [11]. Consequently, a palladium addition to a Cu–50 at. % Au alloy is expected to give rise to a higher activation energy for diffusion. Since the migration energy of a quenched-in vacancy (E_M) is usually about a half of the E value, the E_M values in the alloys examined here are estimated to increase with increasing the palladium concentration. This explains well the experimental results that the rate of low temperature ageing decreased with increasing the palladium concentration.

5. Conclusions

Low temperature ageing at 37° C in an equiatomic CuAu alloy and several Cu–Au–Pd ternary alloys containing palladium up to 21.3 at. % in the CuAu–$Cu_{0.6}Pd_{0.4}$ pseudo-binary system was studied and the following results were obtained.

(1) Age-hardening and decrease in electrical resistivity occurred in an equiatomic CuAu alloy and Cu–Au–Pd ternary alloys containing palladium up to 11 at. % when these alloys were directly quenched into ice brine from 800° C and aged at 37° C.

(2) Low temperature ageing in these alloys was caused by the progress of long-range-ordering in CuAu I type superstructure. This reaction occurred with the aid of quenched-in vacancies.

(3) The rate of low temperature ageing decreased with increasing the palladium concentration. This was attributed to the migration energy of quenched-in vacancies increased with increasing the palladium concentration.

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