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Age-hardening reactions and microstructures of a dental gold alloy with palladium and platinum

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The age-hardening reactions and microstructures of a dental casting gold alloy with some palladium and platinum were investigated by means of hardness tests, X-ray diffractometry, electrical resistivity measurements, and scanning and transmission electron microscopy. Ageing reactions during isothermal annealing were completed by two stages. The first stage corresponded to the formation of a metastable CuAu I phase within grains, and the second stage to a cellular reaction at grain boundaries. The former contributed to the hardening and the latter to the softening. An activation energy of 128 kJ mol^{-1} for hardening was obtained. Two types of cell growth were observed and could be distinguished in terms of the homologous temperature.

1. Introduction

It is well known that type IV dental casting gold alloys are age-hardenable. According to ADAS No. 5 these alloys should contain gold and platinum-group metals of more than 75 wt %. The basic alloy is a ternary type of gold, copper and silver. As greater strength and hardness are required, palladium and/or platinum are added.

Yasuda and co-workers [1, 2] studied the age-hardening of commercial gold alloys with platinum-group metals. They concluded that the age-hardening is attributable to the formation of an ordered phase, CuAu I. However, the overageing was not reported because of their isochronal ageing studies. An isothermal annealing study was needed for more sufficient information.

The aim of this study was to elucidate the isothermal annealing behaviour in order to understand the age-hardening reactions and the microstructures of a dental casting gold alloy with palladium and platinum.

2. Material and methods

The alloy used in this study was a 60 wt % Au–13 wt % Cu–12 wt % Ag–9 wt % Pd–5 wt % Pt–1 wt % Zn (PGA-60, Ishifuku Metal Industry Co., Ltd, Tokyo, Japan). The alloy was first solution-treated at 700° C for 30 min and then quenched into ice brine. Isothermal and anisothermal annealings were carried out at 200, 300, 400 or 500° C for up to 2×10^5 min, and at a heating rate of 0.1° C min^{-1}. The annealing behaviour was observed by means of hardness tests, X-ray diffractometry (XRD), electrical resistivity measurements, and scanning and transmission electron microscopy (SEM and TEM).

The hardness tests were made using a diamond pyramid hardness indentor with a 300 gf load. The Vickers hardness results are the average of five indentations. The XRD studies with nickel-filtered Cu-K_α radiation were done on heat-treated filings. The electrical resistivity measurements were made using the four-terminal potentiometric method at liquid-nitrogen temperature for isothermal annealing specimens and at each temperature in vacuum for anisothermal annealing. Specimens for SEM were prepared using the standard metallographic technique. The final etchant used was a freshly prepared aqueous solution of 10% potassium cyanide and 10% ammonium persulphate. Specimens for TEM were thinned by a jet method. The electrolyte used was a mixture of chromic acid and glacial acetic acid. The SEM and TEM observations were made with microscopes operating at 20 and 200kV, respectively.

3. Results and discussion

3.1. Electrical resistivity

Fig. 1 shows the electrical resistivity changes of the present alloy with temperature during continuous heating and cooling at a rate of 0.1° C min^{-1} after homogenization and then quenching. During the heating a decrease of resistivity due to a phase transformation began at about 225° C. After attaining a minimum, the resistivity increased and changed slope at about 630° C. There was a change of slope at about 570° C on the cooling curve. This suggests a critical temperature (T_c). It is expected that the true T_c exists at a temperature between 570 and 630° C. This behaviour is very similar to that found in previous work [1]. The T_c of their alloy was higher than that of the present alloy because their alloy contained more platinum, which plays a role in raising T_c effectively [3].

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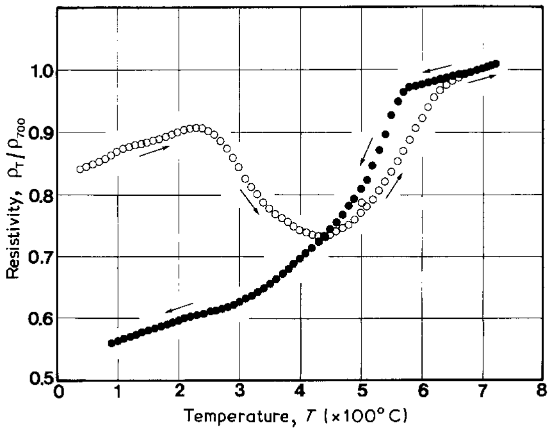

Figure 1 Resistivity change with the temperature during continuous heating or cooling at 0.1° C min^{-1}.

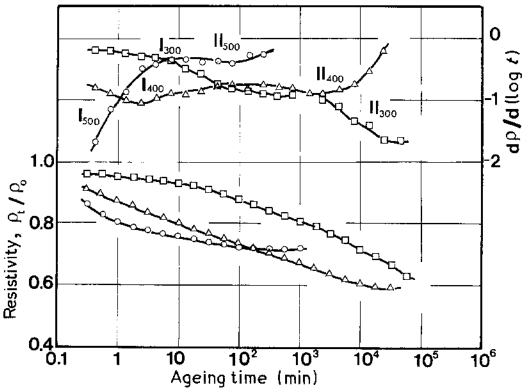

Figure 3 Variations of electrical resistivity and their derivatives with the annealing time. (□) 300° C, (△) 400° C and (○) 500° C.

3.2. Isothermal annealing

Judging from the value of T_c, we had isothermal annealing at 200, 300, 400 or 500° C. The results of the hardness tests are shown in Fig. 2. The hardness value increased with the ageing time, and softening by overageing was obtained after attaining a maximum hardness. The present alloy was greatly hardened by annealing at 300, 400 or 500° C.

Fig. 3 shows variations of electrical resistivity and their derivatives with the ageing time. As indicated in the figure, two stages (I and II) were confirmed at the temperatures of 300, 400 or 500° C. Compared with the hardness data in Fig. 2, it is thought that stages I and II correspond to the hardening and the softening, respectively.

Applying an Arrhenius plot for the time to reach the hardness peak, a straight line was obtained (Fig. 4). An activation energy of 128 kJ mol^{-1} for the hardening reaction was calculated from the slope. This value is nearly equal to that for the migration of copper [4, 5]. This suggests the migration for annihilation of the excess vacancies which were introduced by quenching. It is thought that stage I was attained within grains by migration of copper solute atoms.

3.3. Ageing behaviour at 500° C

Fig. 5 shows SEM images of the specimens aged for (a) 10^2 min, (b) 3.5×10^4 min and (c) 10^5 min at 500° C. Ageing for 10^2 min produced small amounts of grain boundary components, which indicate a typical cellular reaction. The cellular products increased with the ageing time. At longer ageing, growth occurred such as the increase of cellular spacing at the grain boundary, although the growth rate of cell into grains decreased. Similar behaviour has also been observed in a Pb–Cd alloy [6]. Within grains, fine cells were formed after comparatively long ageing times, as seen in Figs 5b and c. In any case, it is obvious that two types of cell reactions at grain boundaries and within grains exist in this alloy.

Fig. 6 shows variations of XRD profiles for the specimen aged at 500° C for various times. After ageing for 1 min, matrix α_0-phase disappeared and some additional lines from new phases were detected. These were identified as an α_2'-phase with f c c and a CuAu I′ ($L1_0$) with f c t. A prime is used to denote the metastable phases. As the lattice constants of the a-axis in α_2' and $L1_0'$ may be nearly equal, the 2 0 0 reflection lines could not be distinguished. With increasing ageing time the diffraction angles of both phases shifted gradually. This change is more obvious in Fig. 7. In the case of $L1_0'$ the 0 0 1 superlattice line moved to the higher- and the 1 1 0 to the lower-angle side. This means that the c-axis of $L1_0'$ shortened and the a-axis elongated continuously with the ageing time. Consequently, the axial ratio as seen in Fig. 7 gradually decreased until about 10^2 min of ageing. Ageing for 3.5×10^4 min produced two phases as seen in Fig. 6. These phases were identified as a silver-rich phase with a = 0.3976 nm and an $L1_0$-type

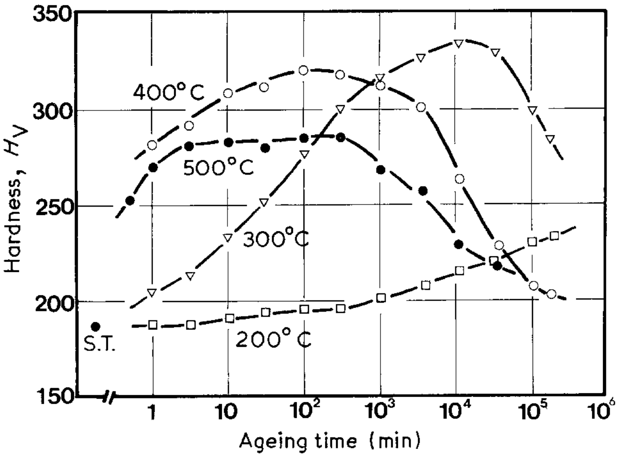

Figure 2 Variations of hardness with the annealing time.

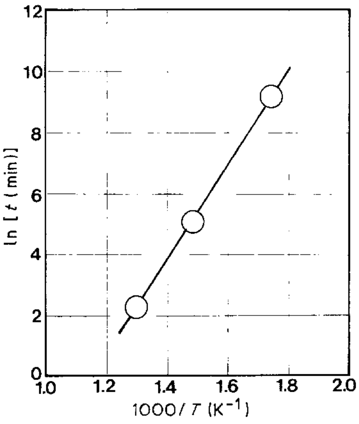

Figure 4 An Arrhenius plot of hardness.

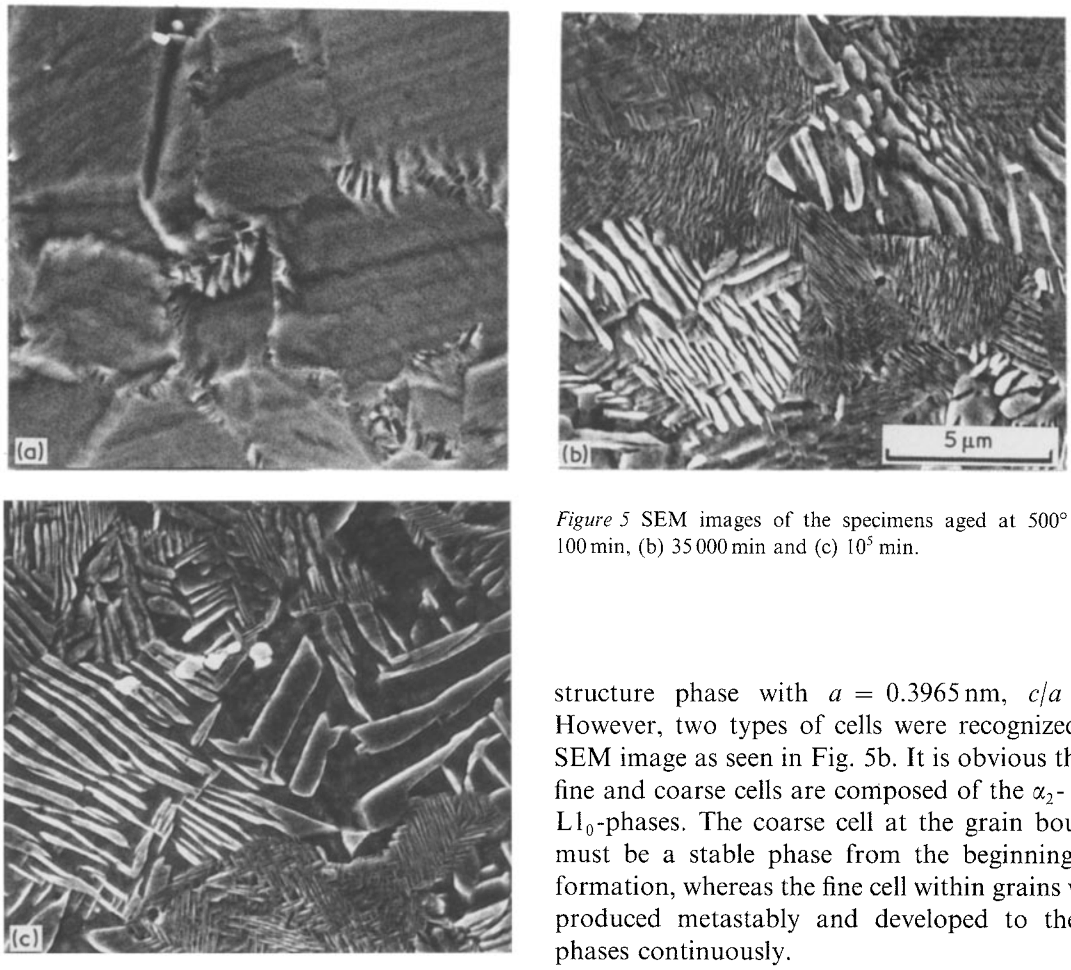

Figure 5 SEM images of the specimens aged at 500° C for (a) 100 min, (b) 35 000 min and (c) 10^5 min.

structure phase with $a = 0.3965$ nm, $c/a = 0.91$. However, two types of cells were recognized in the SEM image as seen in Fig. 5b. It is obvious that both fine and coarse cells are composed of the α_2- and the $L1_0$-phases. The coarse cell at the grain boundaries must be a stable phase from the beginning of cell formation, whereas the fine cell within grains was first produced metastably and developed to the stable phases continuously.

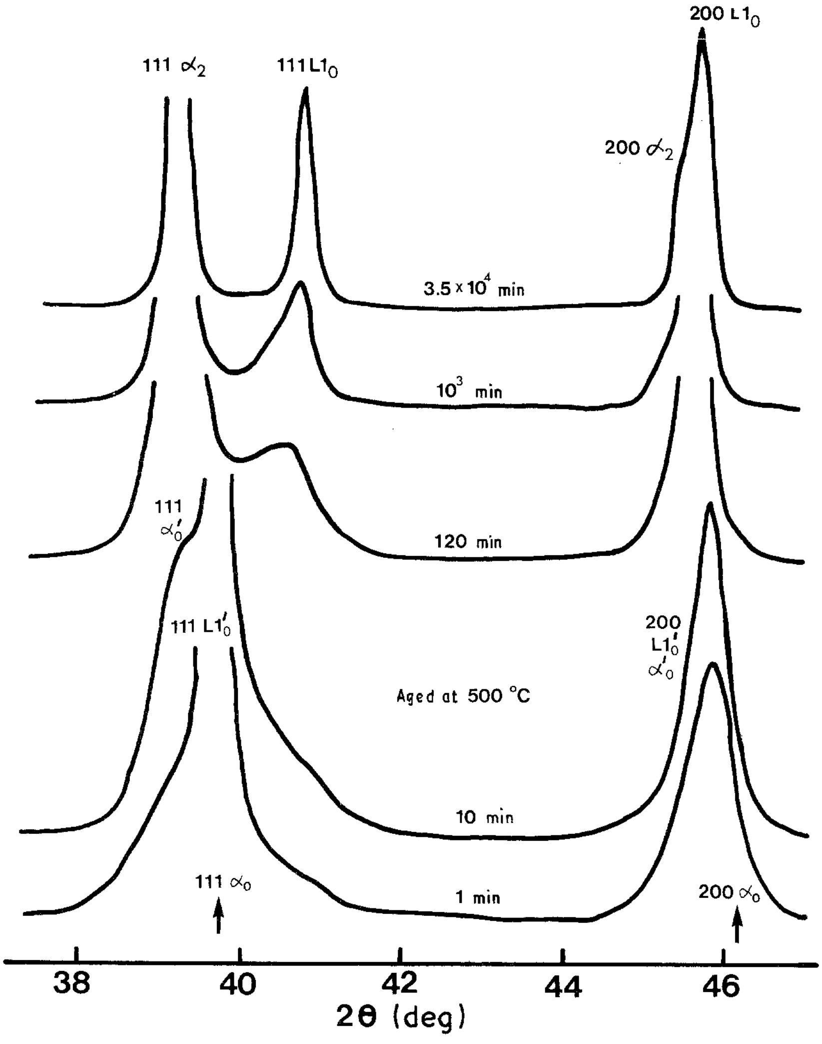

Figure 6 Variations of XRD profiles of the specimen aged at 500° C with the ageing time.

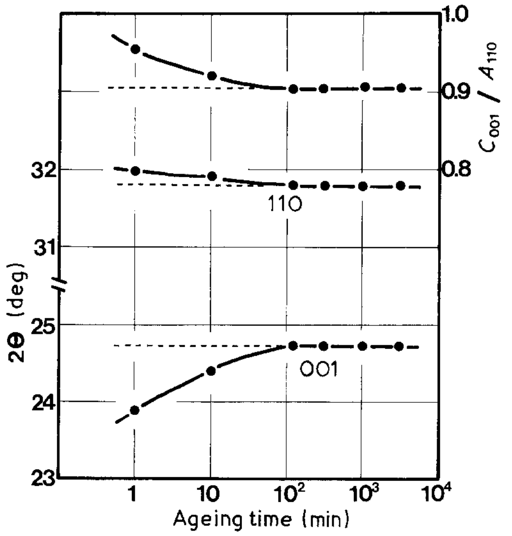

Figure 7 Variations of the diffraction angles and the axial ratio of the specimen aged at 500° C with the ageing time.

Fig. 8 shows $00\,1_X$ dark field (DF) images of the specimens aged at 500° C for 10 min (a) or for 100 min (b), and selected-area electron diffraction (SAD) pattern with [0 0 1] incidence of the latter (c) and its key diagram (d). In the early stage the CuAu I′(L1_0) phase with three variants was produced within grains. The subscripts X, Y and Z in Fig. 8 refer to the spots from L1_0 structures which have their c-axis in the X-, Y- and Z-directions. With increasing time the phase developed and formed platelets, from which the SAD pattern made the streaks seen in Fig. 8c.

This grain interior reaction must contribute to hardening compared with the hardness data in Fig. 2. Yasuda and co-workers [1, 2] have already reported that the hardening is due to the introduction of coherency strain at the interface between CuAu I′ ordered platelets and matrix in a commercial dental alloy.

3.4. Ageing behaviour at 400° C

Fig. 9 shows SEM images of the specimens aged at 400° C for 100 min (a) and 10^5 min (b). Ageing for 100 min at 400° C produced a cellular product, as did ageing at 500° C. No reaction was recognized within the grains in the SEM image. The cell developed into grains with increasing ageing time and finally covered the whole grains as shown in Fig. 9b. The microstructure must correspond to the stable phases of the present alloy at 400° C. However, 100 min of ageing caused a hardness peak as seen in Fig. 2. It is implied that other reactions occurred within grains.

Fig. 10 shows an SAD pattern with [0 0 1] incidence and the $00\,1_X$ DF image of the specimen aged for 100 min. As well as the specimen aged at 500° C, CuAu I′ phase with three variants was found within grains. The early stage at 400° c is analogous to that at 500° C.

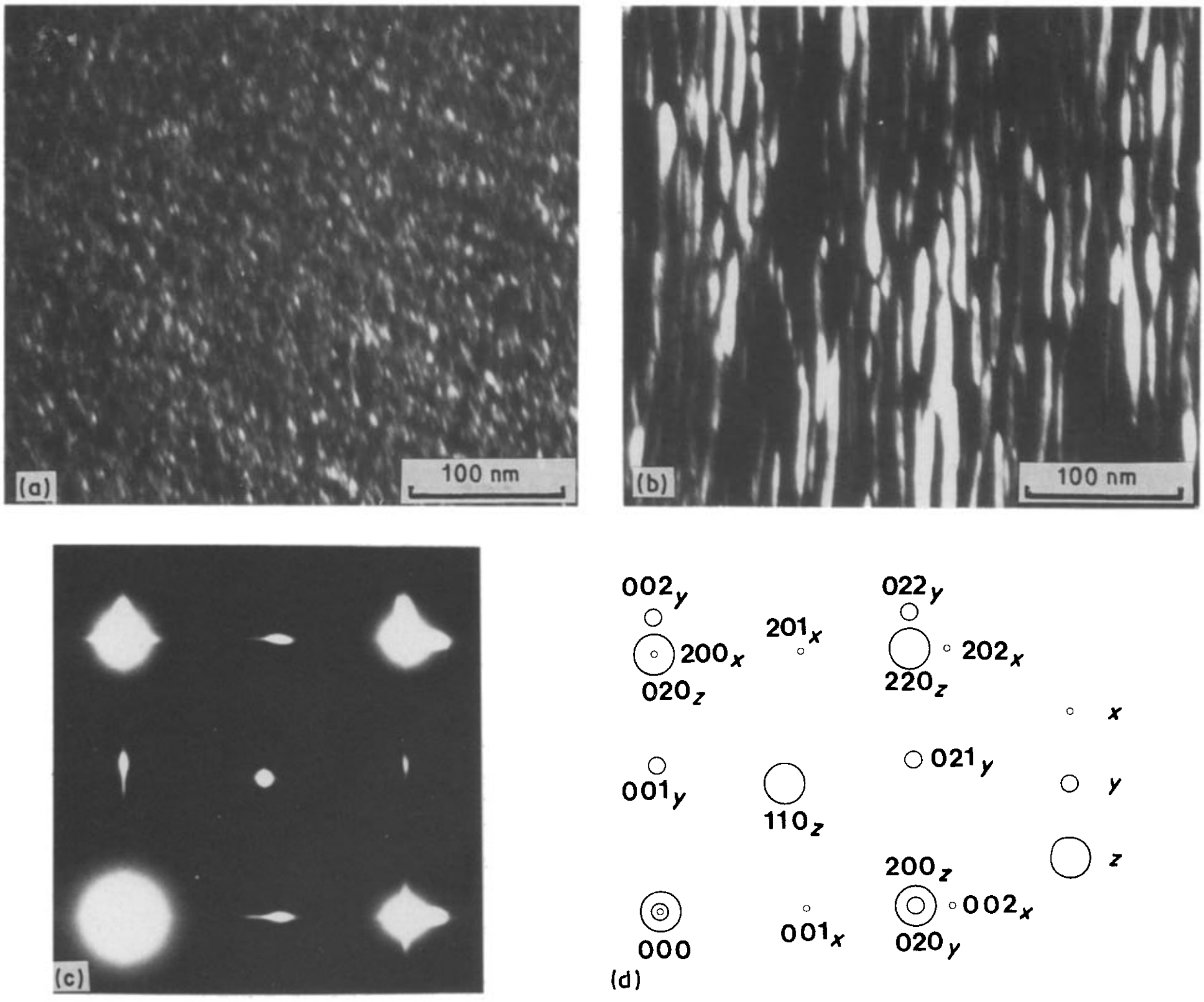

Figure 8 $00\,1_X$ DF images of the specimens aged at 500° C for (a) 10 min or (b) 100 min and SAD pattern with [0 0 1] incidence of the latter (c) and its key diagram (d).

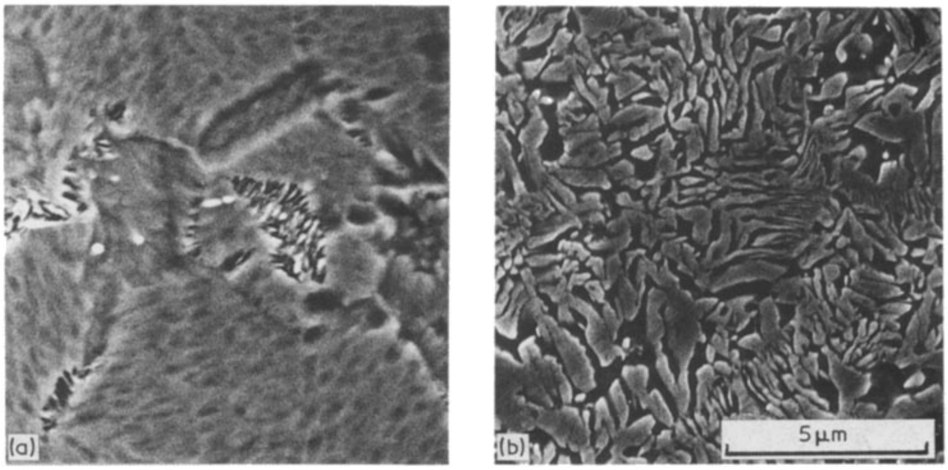

Figure 9 SEM images of the specimens aged at 400° C for (a) 100 min and (b) 10^5 min.

Fig. 11 shows variations of the XRD profile for the specimen aged at 400° C for various times. The following phase relationships were confirmed:

$$\alpha_0(\text{fcc}) \rightarrow \text{CuAu I}' (\text{L}1_0) + \alpha_0' (\text{fcc})$$
$$\rightarrow \text{CuAu I} (\text{L}1_0) + \alpha_2 (\text{fcc})$$

We can conclude that the ageing at 400° C completed by a cellular grain boundary reaction as seen in Fig. 9b via a grain interior reaction as seen in Fig. 10b. The grain interior reaction contributed to hardening and the grain boundary reaction to softening. These reactions must correspond to stages I and II indicated in Fig. 3.

3.5. Factors controlling cell growth

Although similar reactions were observed by XRD at both 400 and 500° C, each microstructure was very different. At both ageing temperatures it is evident that a grain boundary reaction and a grain interior reaction occurred. At the lower temperature (400° C) the growth of grain boundary components predominates, whereas at the higher temperature (500° C) the growth of grain interior components predominates. The latter, therefore, produced both fine and coarse cells and the former was covered with the cells from grain boundaries. It is therefore suggested that the latter is a lattice diffusion-controlling reaction and the former is a grain boundary one. Hirschhorn and Gregg [7] distinguished diffusion-controlled growth of discontinuous precipitation in terms of the homologous temperature (T_H). The ratio of the annealing temperature to the liquidus temperature (T_m) of the specimen, T/T_m, is an important value. In their opinion, when $T > 0.6T_\text{m}$ the dominant reaction of growth is of lattice diffusion-controlled type and when $T < 0.5T_\text{m}$ it is of grain boundary diffusion-controlled type. Nozato and Tsubakino [8] also made a similar study for a Pb–1.5 wt % Cd alloy. They reported that a temperature of 70° C separated the reaction into two types of discontinuous precipitations. Above 70° C it was controlled by lattice diffusion, and below 70° C it was controlled by grain boundary diffusion. In this case the ratio was 0.57 at 70° C. In the present specimen the value could be calculated to be 0.63 for a 500° C anneal and 0.54 for a 400° C anneal. Consequently, it must be reasonable that at 500° C the lattice diffusion-controlled reaction occurs and at 400° C the grain boundary diffusion-controlled reaction occurs.

4. Conclusion

The age-hardening reactions and the microstructures of a dental casting gold alloy with some palladium and platinum were studied by hardness tests, XRD,

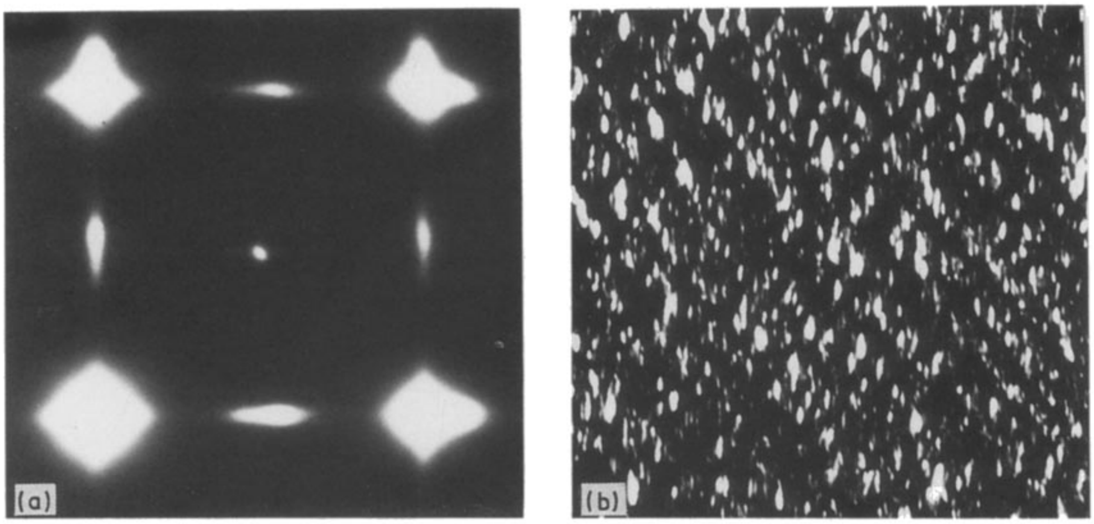

Figure 10 (a) SAD pattern with [1 0 0] incidence and (b) $0\,0\,1_\chi$ DF image of the specimen aged at 400° C for 100 min.

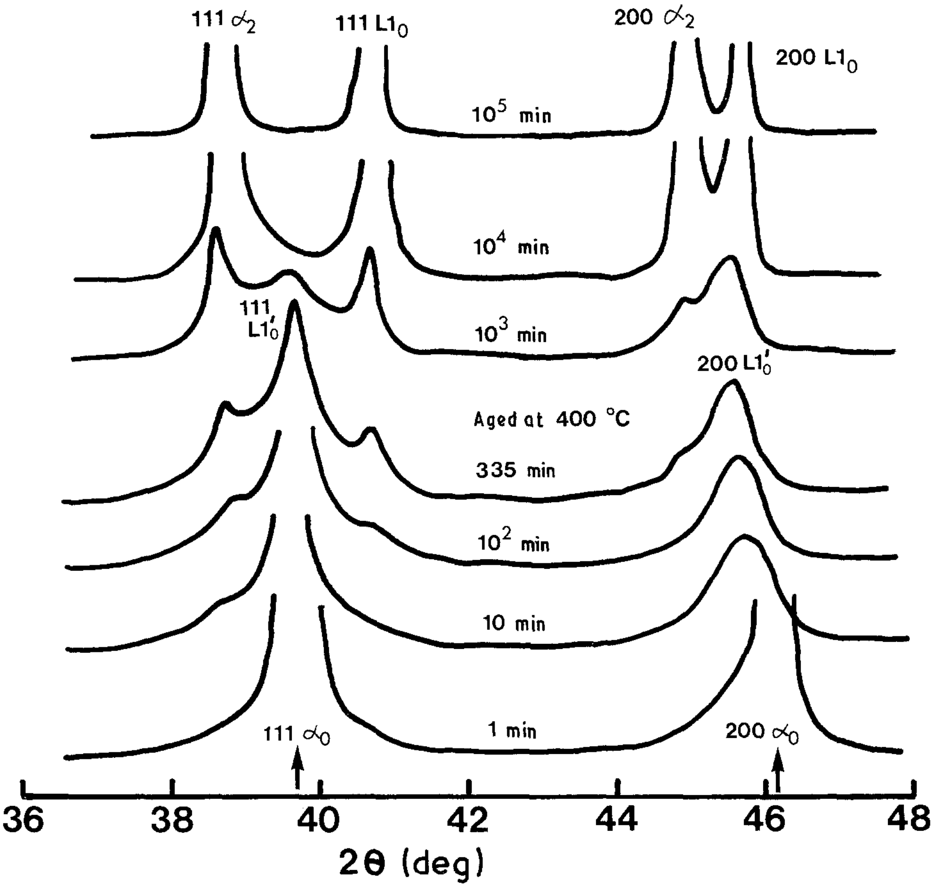

Figure 11 Variations of XRD profile of the specimen aged at 400° C with the annealing time.

electrical resistivity measurements, SEM and TEM observations. The main results are as follows.

1. Phase transformation was completed by stages I and II, which correspond to the formation of CuAu I′ within grains and a cellular reaction at grain boundaries, respectively. The former contributed to the hardening and the latter to the softening.

2. There were two types of cell growth, depending on the annealing temperature. The homologous temperature was an indicator for distinguishing the diffusion-controlled reaction for cell growth.

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