

Age-hardening associated with precipitation reaction and spinodal decomposition in a commercial dental low-carat Au–Ag–Cu–Pd alloy

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Two distinguishable hardening mechanisms, depending on the temperature, were found by isothermal ageing in a commercial dental low-carat Au–Ag–Cu–Pd alloy. Age-hardening was attributed to the precipitation of the metastable AuCu I' and equilibrium AuCu I ordered phases and spinodal decomposition depending on the ageing temperature. It was clearly visible, by using the direct-ageing method, that the XRD peaks of the parent phases showed a shift during transformation.

1. Introduction

Although conventional dental casting gold alloys should contain noble metals of more than 75 wt % according to American Dental Association specification No. 5, alternative low-carat gold alloys are currently widely used for dental cast restorations. Conventional dental casting gold alloys are essentially ternary alloys of gold, silver and copper. However, low gold content dental alloys contain some quantity of palladium to preserve the tarnish and corrosion resistance. It is well known that the ternary Au–Ag–Cu alloys show significant age-hardening in a certain composition region by appropriate heat treatment and that the addition of palladium to the ternary Au–Ag–Cu system gives rise to conspicuous age-hardening.

The ternary Au–Ag–Cu system is characterized by ordered regions and a two-phase decomposition region. Thus, the hardening mechanism of the ternary Au–Ag–Cu alloys is thought to be due to phase transformation such as ordering, precipitation and spinodal decomposition [1–7], depending on the composition of the alloy and on the ageing temperature.

It was reported that the addition of palladium to the ternary Au–Ag–Cu system led to the elevation of the critical temperature of the AuCu I ordering, and that the hardening of the dental low-carat Au–Ag–Cu–Pd alloys was caused by the AuCu I ordering or AuCu I' ordering [8–10]. However, because of their complex combinations of constituents age-hardening mechanisms have not yet been sufficiently elucidated. The present study was conducted to investigate the sequence of phase transformation associated with isothermal age-hardening in the dental low-carat Au–Ag–Cu–Pd alloy depending on the ageing temperature.

2. Materials and methods

The specimen alloy used in the present study was a commercial dental gold alloy of nominal composition 58.0 wt % Au–23.3 wt % Ag–12.0 wt % Cu–5.5 wt % Pd (Stabilor-G Alloy, Degussa, Germany). The atomic composition of this alloy was calculated from the nominal composition to be 39.2 at % Au–28.8 at % Ag–25.1 at % Cu–6.9 at % Pd.

A powder specimen, which was prepared by filing the alloy, was vacuum-sealed in a silica tube and was then solution-treated at 750 °C for 30 min and quenched after solution treatment by dropping it into a beaker of ice brine. Differential thermal analysis (DTA) was made on the solution-treated powder specimen from room temperature to 600 °C using a DTA apparatus (SSC/5200 S II, Seiko instruments Inc., Japan), to obtain general information on the structural transformations. DTA was performed at a heating rate of 10 °C min⁻¹ under a nitrogen atmosphere.

Plate specimens for the hardness test were first solution-treated at 750 °C for 30 min under an argon atmosphere and then quenched into ice brine to obtain a supersaturated solid solution, and were subsequently aged in a molten salt bath at temperatures at which exothermic peaks were observed in the DTA curve and then quenched into ice brine. The hardness measurements were made on plate specimens which had been subjected to heat treatment at given ageing temperatures for various times, using a micro-Vickers hardness tester with a 300 gf load and a 10 s holding time. Vickers hardness results were obtained as the average values of five measurements.

Powder specimens, which were prepared by filing the alloy, for X-ray diffraction (XRD) study were vacuum-sealed in a silica tube and then were subjected to the required heat treatment. XRD study was carried

out on the heat-treated powder specimens using an X-ray diffractometer (Rigaku Denki Co. Ltd., D/Max-2400, Japan). The X-ray diffractometer was operated at 40 kV and 50 mA. Nickel-filtered $\text{CuK}\alpha$ radiation was used as the incident beam.

3. Results and discussion

Fig. 1 shows the DTA curve obtained by heating the solution-treated powder specimen from room temperature to 600 °C. Three exothermic peaks at 324.9, 452.4 and 551.7 °C were observed in the temperature range studied. It can be seen from the DTA result that three types of transformation occur between room temperature and 600 °C.

Fig. 2 represents the change of hardness during isothermal ageing at 325, 450 and 550 °C. These temperatures were determined from the DTA result. A supersaturated solid solution of the specimen alloy exhibited remarkable hardening by ageing at 325 and 450 °C. The hardness started to increase rapidly at the initial ageing stage, and then continued to rise gradually to maximum hardness for a time. A drastic softening was observed after showing maximum hardness. When the specimen was aged at 550 °C, on the other hand, significant age-hardening was not observed.

Fig. 3 shows the XRD patterns of the powder specimens solution-treated at 750 °C for 30 min and aged at selected temperatures for 10 000 min. The solution-treated specimen gives an XRD pattern of the α_0 single phase with a face centred cubic (fcc) structure. The α_0 single phase of the solution-treated specimen was finally transformed into the Ag-rich α_1 and Cu-rich α_2 phases with a fcc structure by ageing at 550 °C. By ageing at 325 and 450 °C, the Ag-rich α_1 phase with a fcc structure and the AuCu I ordered phase with a face centred tetragonal (fct) structure were finally formed. These results suggest that an

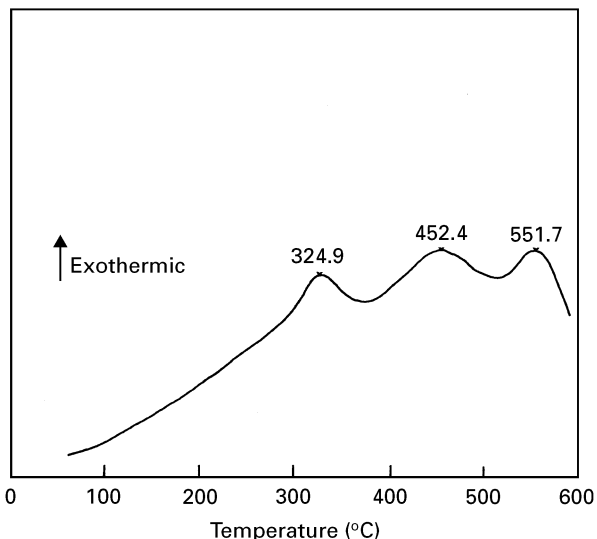


Figure 1 DTA curve obtained by heating the solution-treated powder specimen from room temperature to 600 °C. Heating rate was 10 °C min⁻¹.

exothermic peak of 551.7 °C in the DTA curve corresponds to the transformation $\alpha_0 \rightarrow \text{Ag-rich } \alpha_1 + \text{Cu-rich } \alpha_2$, and two exothermic peaks of 324.9 and 452.4 °C correspond to the transformation $\alpha_0 \rightarrow \text{Ag-rich } \alpha_1 + \text{AuCu I}$.

Significant age-hardening occurred by ageing of the solution-treated specimen at 325 and 450 °C, at which the Ag-rich α_1 and AuCu I ordered phases were formed stably by ageing, as can be seen in the isothermal age-hardening curves (Fig. 2) and the XRD patterns of the specimens aged for 10 000 min (Fig. 3). Although the same stable phases were formed by ageing at 325 and 450 °C, two distinguishable peaks were observed in the DTA curve. Accordingly, it can be expected that the sequences of transformation are different from each other.

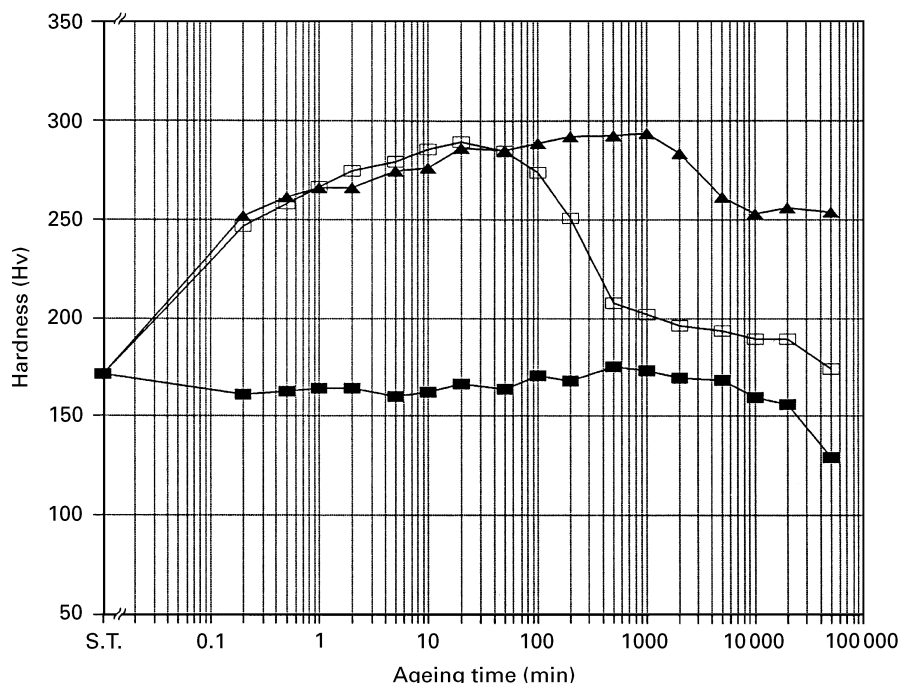


Figure 2 Isothermal age-hardening curves at 325 (▲), 450 (◻) and 550 °C (■).

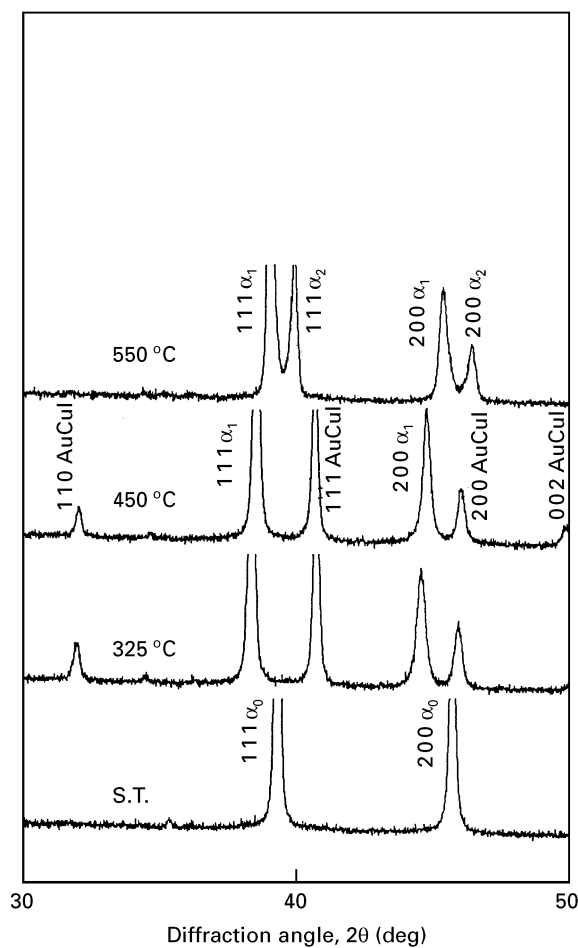


Figure 3 XRD patterns of the specimens solution-treated at 750 °C for 30 min and aged for 10000 min at 325, 450 and 550 °C.

To identify the sequence of phase changes during isothermal ageing at 325 and 450 °C, XRD patterns were taken from the powder specimens aged for the various times. Fig. 4 represents the changes in the XRD pattern during isothermal ageing at 450 °C for various periods. By ageing at 450 °C, the metastable Ag-rich α_1' and AuCu I' ordered phases were formed from the supersaturated α_0 phase prior to the final formation of the equilibrium Ag-rich α_1 and AuCu I ordered phases. As seen in Fig. 4, the 111 diffraction peaks of the metastable Ag-rich α_1' and AuCu I' ordered phases were separated, while the 200 diffraction peaks of both phases were superimposed. This means that the metastable AuCu I' ordered phase has the fct structure with a lattice parameter, a , similar to that of the metastable Ag-rich α_1' phase with a fcc structure.

The 111 diffraction peak of the supersaturated α_0 phase decreases in intensity with the formation of the metastable Ag-rich α_1' and AuCu I' ordered phases, and then the 111 diffraction peak of the metastable Ag-rich α_1' phase decreases in intensity with the formation of the equilibrium Ag-rich α_1 and AuCu I ordered phases. Moreover, the diffraction peaks of the metastable Ag-rich α_1' phase and the equilibrium Ag-rich α_1 phase have a low diffraction angle in comparison with those of the α_0 phase and the metastable Ag-rich α_1' phase, respectively. This transformation process seems to be brought about by the precipitation of the ordered phases in the supersaturated matrix. With precipitation of the metastable AuCu I' ordered phase in the α_0 phase and the equilibrium

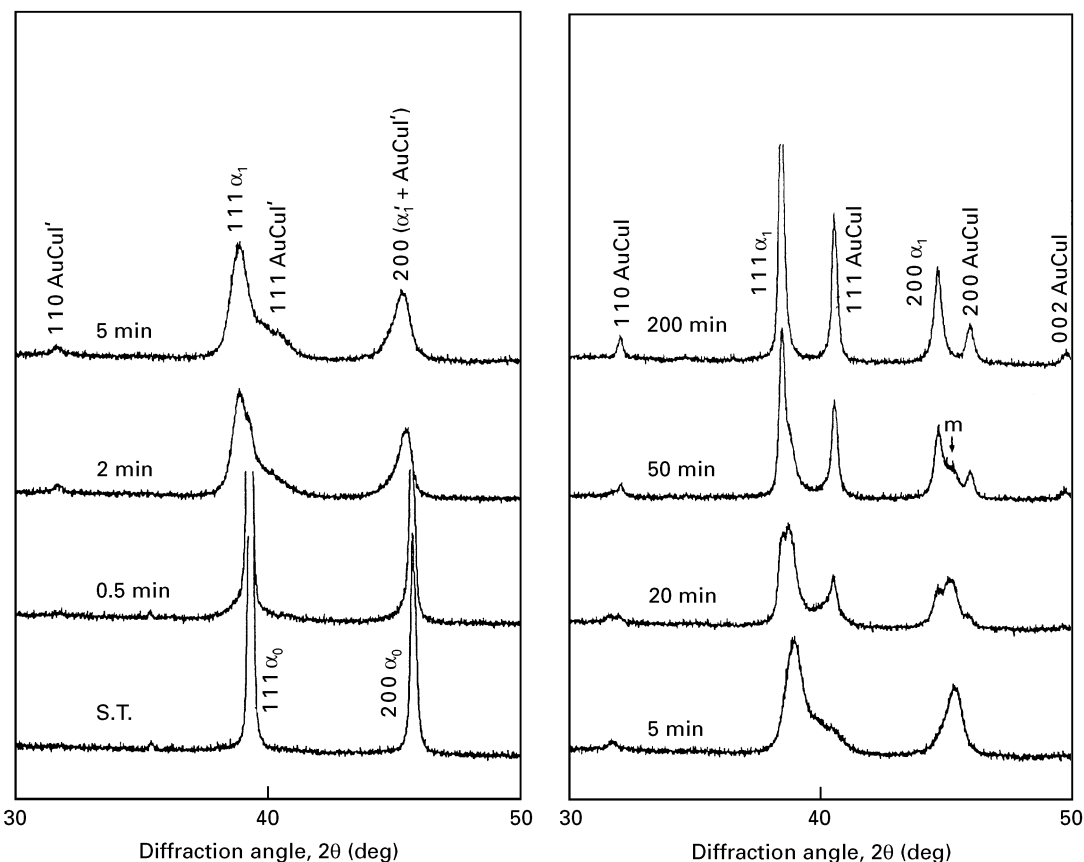


Figure 4 Changes in the XRD pattern during isothermal ageing at 450 °C. (The mark m indicates the 200 diffraction peaks of the metastable α_1' and AuCu I' phases.)

AuCu I ordered phase in the metastable Ag-rich α_1' phase, the metastable Ag-rich α_1' phase and the equilibrium Ag-rich α_1 phase will be formed. These contain a little lower percentage of copper than the α_0 phase and the metastable Ag-rich α_1' phase, respectively. The atomic size of copper is smaller than those of the other atoms. Consequently, the position of the diffraction peaks of the metastable Ag-rich α_1' phase and the equilibrium Ag-rich α_1 phase move to the low diffraction angle as a result of the lattice parameter changes.

In addition, the diffraction peaks of the α_0 phase and the metastable Ag-rich α_1' phase show a shift toward the low diffraction angle during hardening, as can be seen in the isothermal age-hardening curves (Fig. 2) and the changes in the XRD pattern (Fig. 4). The shift of the diffraction peaks results from the lattice strain caused by the variation in composition. This shift provides evidence against a homogeneous mechanism in the transformation. Therefore, it could be thought that the transformation at 450 °C occurred homogeneously by the precipitation reaction of the ordered phases. In most systems transformed by a precipitation, the final stable phases have such different crystal structures that it is impossible to form coherent interfaces and the homogeneous nucleation of the equilibrium phase is then impossible. However, it is often possible to form a coherent nucleus of a metastable phase [11].

Thus, it can be considered that the age-hardening at 450 °C is attributed to the lattice strain of the super-saturated α_0 phase resulting from the precipitation of the metastable AuCu I' ordered phase, and to the

lattice strain of the metastable Ag-rich α_1' phase resulting from the precipitation of the equilibrium AuCu I ordered phase. Yasuda and Kanzawa [8] observed in an experimental gold alloy (37.1 at % Au–17.8 at % Ag–35.4 at % Cu–9.7 at % Pd) that the age-hardening was due to the strain induced by the formation of AuCu I ordered nuclei in the matrix. Yasuda *et al.* [9] found in commercial dental 16 and 14 carat gold alloys containing palladium that the metastable AuCu I' ordered phase was formed by ageing and that the age-hardening was due to the introduction of coherency strain at the interface between the metastable AuCu I' ordered platelets and the matrix.

On the other hand, quite different changes in the XRD pattern were observed by ageing at 325 °C, although the Ag-rich α_1 and AuCu I ordered phases were finally formed from the α_0 phase at 450 °C. Fig. 5 represents the changes in the XRD pattern during isothermal ageing at 325 °C for the various periods. XRD patterns of the powder specimens aged at 325 °C seem to exhibit side-bands in the early stage of ageing, which accompany the 111 diffraction peak of the α_0 phase. The weak and broad side-band peak of the low angle side moves closer to the main reflection with progress in ageing, as indicated by lines in Fig. 5, although the side-band peak of the high angle side does not indicate a clear approach to the main reflection. The 110 diffraction peak of the metastable AuCu I' ordered phase appeared concurrently shortly after, followed by the appearance of the side-band peaks [12]. The weak and broad side-band peaks do not become intense during the simultaneous appearance of the diffraction peaks of the metastable phases. With

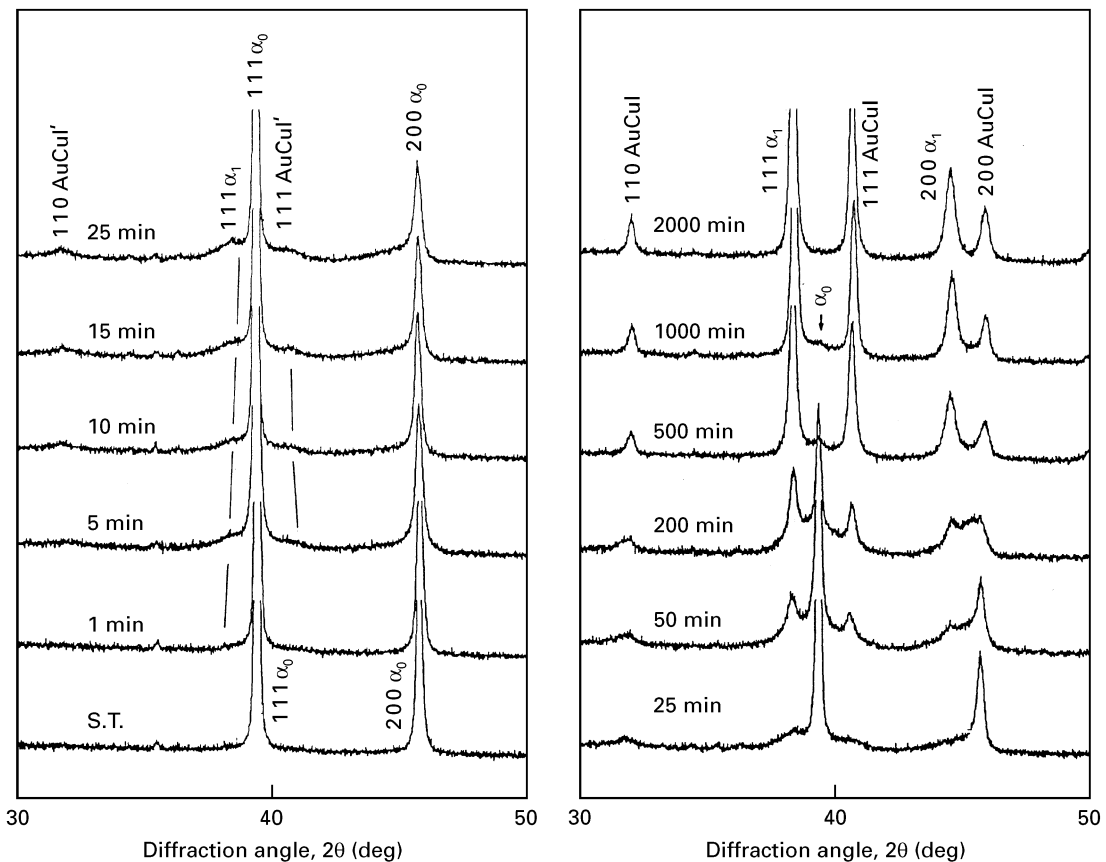


Figure 5 Changes in the XRD pattern during isothermal ageing at 325 °C.

further ageing, the side-band peaks were completely hidden and could not be distinguished after the appearance of the diffraction peaks of the equilibrium phases. However, the side-bands could not be found around the 200 diffraction peak of the α_0 phase. The spinodal mode of transformation was also observed in the low-carat Au–Ag–Cu ternary alloys [2–5, 7].

The phase transformation sequence at 325 °C can be considered, from the results obtained by the XRD study, to be as follows. The supersaturated α_0 phase was decomposed by spinodal decomposition prior to the formation of the metastable Ag-rich α_1' and AuCu I' ordered phases, and then these metastable phases finally transformed to the equilibrium Ag-rich α_1 and AuCu I ordered phases with further ageing. The α_0 phase which seemed to be decomposed by spinodal decomposition existed during the increase in hardness, as seen in the isothermal age-hardening curves (Fig. 2) and the changes in the XRD patterns (Fig. 5). Therefore, it can be considered that the age-hardening at 325 °C is generated by association with spinodal decomposition.

Additionally, the diffraction peaks of the α_0 phase showed a slight shift toward both the high and low diffraction angles during the occurrence of spinodal decomposition. The shift of the diffraction peaks of the α_0 phase was also observed in a Au–49.7 at % Cu–15.8 at % Ag alloy during the process of spinodal decomposition by Yasuda and Ohta [2]. However, they did not document such a mode.

Age-hardening is achieved by a suitable ageing operation, following the quenching of the solution-

treated specimen to create a supersaturated condition, and is caused by the phase transformation resulting from the ageing of the supersaturated single phase alloy formed by solution treatment. When an alloy is rapidly quenched from a high solution treatment temperature to ice brine temperature, excess vacancies are retained during quenching. These supersaturated quenched-in vacancies can assist nucleation, so that many nuclei may form during quenching or right at the beginning of ageing, although additional nucleation continues to occur throughout the transformation.

In order to get more information about the process of the phase separation at the beginning of, and during, transformation changes in the XRD pattern during isothermal direct ageing at 325 and 450 °C were examined on the powder specimens. The solution-treated powder specimens were quenched directly into a salt bath and aged for various times. This direct-ageing method will reduce the rapid nucleation which is achieved by the consumption of quenched-in excess vacancies retained during rapid quenching into ice brine.

Fig. 6 represents the changes in the XRD pattern during direct ageing at 450 °C for various periods. The mark, m, in Fig. 6 indicates the 200 diffraction peaks of the metastable α_1' and AuCu I' phases. In comparison with the results of the changes in the XRD pattern during indirect ageing (Fig. 4), a longer time was required for transformation by direct ageing than by indirect ageing. This delayed reaction is expected since the rapid nucleation was inhibited by direct ageing. It

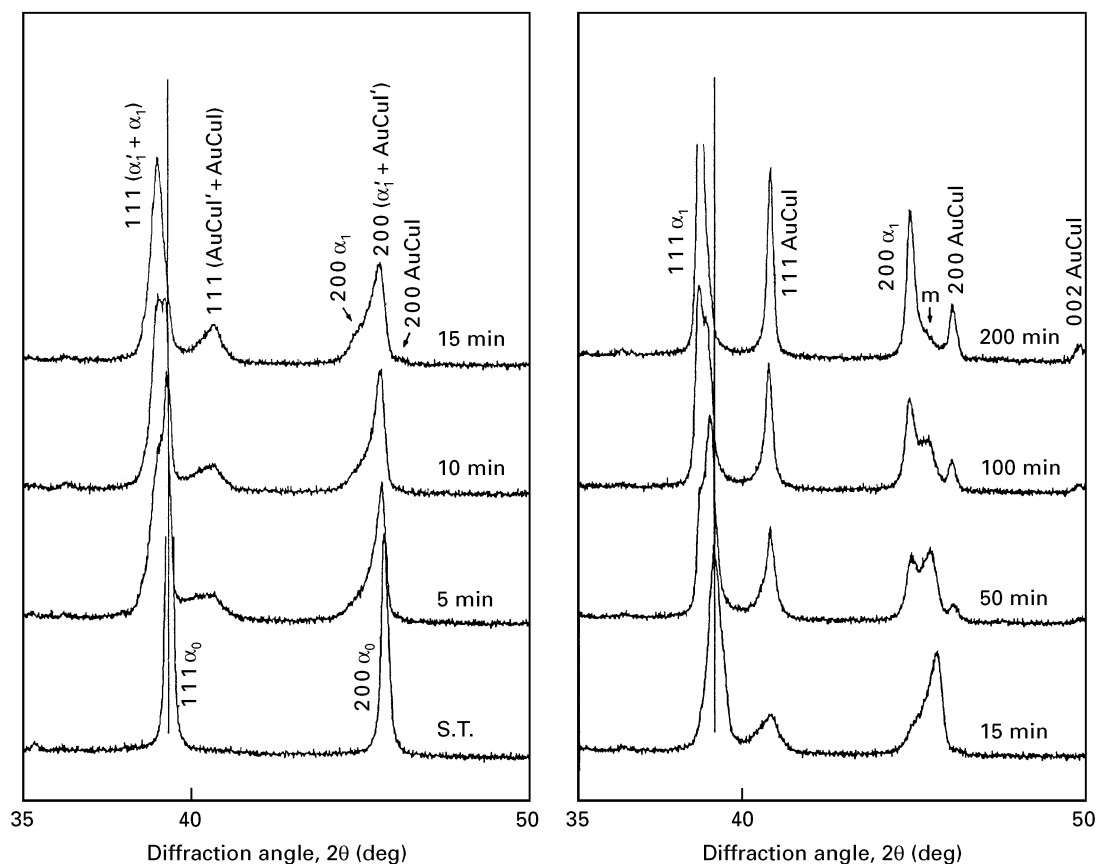


Figure 6 Changes in the XRD pattern during direct ageing at 450 °C. (The mark m indicates the 200 diffraction peaks of the metastable α_1' and AuCu I' phases.)

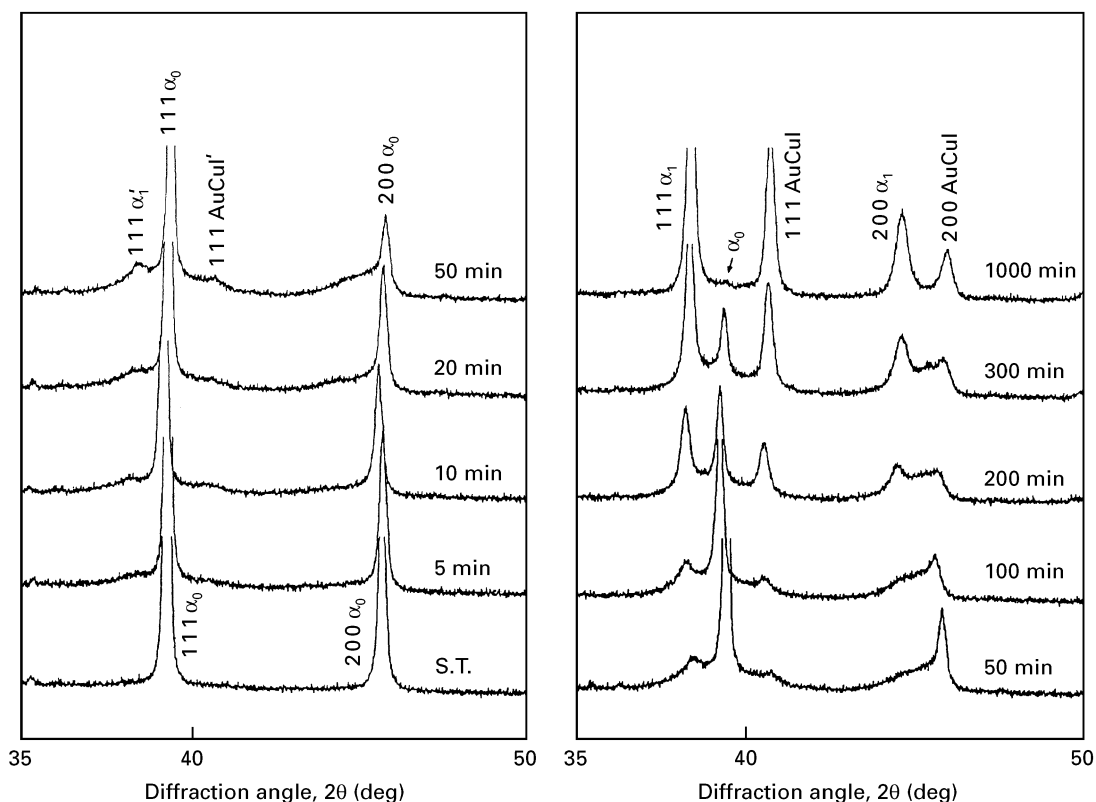


Figure 7 Changes in the XRD pattern during direct ageing at 325 °C.

is clearly visible that the transformation during ageing proceeds by a precipitation process and that the diffraction peaks of the α_0 phase and the metastable Ag-rich α'_1 phase show an apparent shift continuously toward the low diffraction angle during ageing. The continuous shift of the diffraction peaks toward the low diffraction angle can be explained as follows. By the precipitation of the metastable AuCu I' and equilibrium AuCu I ordered phases, the solute contents of Au and Cu atoms in the supersaturated matrices decreases. Cu atoms with smaller atomic size drain out of the surrounding matrix until the α_0 phase becomes the metastable phases, and the metastable phases become the equilibrium phases. As a consequence, the diffraction peaks of the α_0 phase and the metastable AuCu I' ordered phase shift continuously toward the low diffraction angle.

Fig. 7 represents the changes in the XRD pattern during direct ageing at 325 °C for various periods. The overall rate of transformation was not affected by the ageing method. The α_0 phase was observed until 1000 min by direct ageing, like the results obtained by the indirect-ageing method. Therefore, it is obvious that the transformation at 325 °C in this alloy proceeds by a spinodal reaction rather than a nucleation-and-growth reaction.

In addition, it is clearly observed that the shift of the diffraction peaks of the α_0 phase become more apparent by direct ageing. The diffraction peaks of the α_0 phase shifted from a high diffraction angle to a low diffraction angle and vice versa by ageing at 325 °C. Although we cannot fully explain the reason for the shift, such a shift could be thought to be due to additional phase separation [13], and the magnitude

of an initial modulation in composition was affected by the quenching rate [14]. However, the formation of the additional phase was not identified from the results of XRD study.

4. Conclusion

The age-hardening mechanism in a commercial dental low-carat Au–Ag–Cu–Pd alloy was studied by means of DTA, hardness test and XRD study. The following results were obtained.

Significant age-hardening occurred by isothermal ageing at the temperatures at which the Ag-rich α_1 and AuCu I ordered phases were formed stably by ageing. Two distinguishable types of hardening mechanism, depending on the temperature, were found by isothermal ageing in this alloy. When the alloy was aged at 450 °C, the age-hardening was attributed to the formation of the metastable AuCu I' and equilibrium AuCu I ordered phases in the matrix by a precipitation reaction. When the alloy was aged at 325 °C, the age-hardening was generated by association with spinodal decomposition.

The shift of the XRD peaks of the parent phases during transformation was clearly visible by using the direct-ageing method.

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