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# Analytical electron microscopy of cast Au–Ag–Cu alloys

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The microstructure in an as-cast Au–Ag–Cu–Pd alloy has been examined by electron microscopy (TEM) combined with quantitative X-ray microanalysis (EDS). The primary phase formed during solidification is enriched in silver and palladium, while gold and copper segregate to grain boundaries, where substantial amounts of lamellar eutectic colonies are formed. The compositions of the lamellae were determined by EDS analysis to be 56% Au–13% Ag–26% Cu–6% Pd and 50% Au–42% Ag–5.5% Cu–2.5% Pd (wt%). Ordering and decomposition reactions take place during cooling in the solid state: plate-like precipitates of tetragonal AuCu-I on {0 0 1} planes were found within the primary phase and in silver-rich lamellae in eutectic colonies.

## 1. Introduction

Au–Ag–Cu alloys are used in jewellery and in electrical and dental applications. Because of the high price of gold it is desirable to reduce the gold content. This is not straightforward, however, because the corrosion properties may be adversely affected. Materials with a low gold content have been observed to possess a tendency to surface compound formation in aqueous solutions containing sulphides, causing a discoloration or tarnishing of the material [1]. Tarnishing is detrimental in electrical contacts and undesirable in dental applications due to cosmetic considerations.

The corrosion properties of Au–Ag–Cu alloys are, besides composition, to a large extent determined by the microstructure. Surveys of the equilibrium phases formed at 500° C and their effect on tarnish formation have been published [2–4]. A review of microstructures in Au–Ag–Cu–Pd alloys has been given by Yasuda [5]. A brief summary is presented here.

The solidification microstructure is heavily cored. The material that solidifies first is enriched in silver and palladium, while gold and in particular copper segregate to grain-boundary areas and interdendritic regions where substantial amounts of a non-equilibrium lamellar eutectic is formed [2]. During subsequent cooling in the solid state the matrix suffers a decomposition and thus the ordered phase AuCu-I is formed as thin platelets parallel to {0 0 1} planes of the f c c matrix [2]. The AuCu-I phase and most of the lamellae are dissolved by a short anneal at around 700° C. The decomposed matrix and the lamellae in the eutectic structure most likely constitute local galvanic cells. Furthermore the silver-rich phases have been observed to be prone to tarnishing. On the other hand copper in Au–Cu-rich phases is selectively dissolved in aqueous solutions, leaving behind a gold-enriched surface without sulphide formation [6].

Since many of the important structural features in Au–Ag–Cu–Pd alloys are small, transmission electron microscopy (TEM) is necessary to characterize the microstructure in detail. Furthermore, using X-ray energy-dispersive spectroscopy (EDS) in the electron microscope, quantitative chemical analysis at high spatial resolution may be obtained. The aim of the current investigation was to apply the EDS technique in combination with TEM to a commercial dental low-gold alloy.

## 2. Material

The material investigated was a commercial Au–Ag–Cu alloy for dental applications (Midigold, by BEGO, Bremer Goldschlägerei, Wilh. Herbst GmbH). The chemical composition was determined by emission spectrography (Table I). The gold content was checked by additional chemical analysis which gave the somewhat lower value 49.6 wt % Au. The procedure for investment casting and the microstructure of the as-cast material have previously been reported [2].

## 3. Experimental procedure

Samples for transmission electron microscopy were prepared by mechanical grinding followed by jet-polishing at 10° C with an electrolyte consisting of 35 g $CrO_3$ in 200 ml $CH_3COOH$ and 10 ml $H_2O$. Finally ion-beam thinning was carried out. The foils were examined in a JEOL 2000 FX transmission electron microscope equipped with a Tracor Northern 2000 X-ray detector and analyser. EDS was carried out in the TEM mode using a spot size of 10 to 20 nm. Chemical compositions were calculated by using the well-known thin-film approximation [7]

$$\frac{C_A}{C_B} = k_{A,B}\frac{I_A}{I_B} \qquad (1)$$

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TABLE I Composition of material (Midigold)

| Method of analysis | Composition (wt %) | | | | | | |
|---|---|---|---|---|---|---|---|
| | Au | Pt | Ag | Pd | Zn | Cu | In |
| Spectrographic | 54.0 | – | 31.0 | 4.1 | – | 9.4 | 1.0 |
| Chemical | 49.6 | – | – | – | – | – | – |

where $C_A$, $C_B$ denote weight fractions and $I_A$, $I_B$ denote X-ray intensities; $k_{AB}$ is a correction factor to be determined. In the current investigation gold was chosen as the reference Element B in Equation 1 and $I_B$ denotes the intensity of the Au$L\alpha$ line. For the elements, silver, copper and palladium the $K\alpha$ line was used in the calculation.

The correlation factors $k_{A,B}$ were determined experimentally, because considerable errors may be expected in the calculated factors when $L$ lines are involved. Three alloys were used for determination of these factors: (a) 57.1 wt % Au–42.9 wt % Cu, (b) 43.9 wt % Au–56.1 wt % Ag and (c) 59.5 wt % Au–20.5 wt % Ag–15.5 wt % Cu–3.7 wt % Pd. The pure compositions of alloys (a) and (b) are based on the weights of the pure metallic elements. These were melted together in vacuum at 1000° C. Alloy (c) was commercial. The solidified alloys were annealed at 700° C for 70 h in a vacuum, adapted to produce a single-phase structure and to minimize any concentration gradients of the alloy elements. The homogeneity of the materials was verified by electron microprobe analysis. Alloys (a) and (b) gave $k_{Cu} = 0.365$ and $k_{Ag} = 1.661$, respectively, and from Alloy (c) the value $k_{Pd} = 1.488$ was derived. Thus a consistent set of correction factors was established and used for subsequent quantitative analysis.

The Tracor Northern system is equipped with software for calculating $k$ factors, and the values computed in the present case were $k_{Cu} = 0.418$, $k_{Ag} = 1.605$ and $k_{Pd} = 1.489$. The calculated factors fit reasonably well with those experimentally determined.

All X-ray microanalysis was performed in a low-background carbon holder. Thus X-ray spectra with negligible peaks from the instrument and the specimen environment were obtained.

## 4. Results

A micrograph illustrating the two dominant features in the alloy is shown in Fig. 1. On the right-hand side is the pre-eutectic matrix with a high density of fine plate-like precipitates. These precipitates were probably formed in the solid state during cooling to room temperature. On the left-hand side is shown a lamellar eutectic colony. Optical microscopy also revealed that the alloy contains substantial amounts of eutectic colonies at grain boundaries [2]. The eutectic morphology is described as alternating lamellae of two phases. The lamellae are of the order of 0.03 $\mu$m thick and several micrometres long.

X-ray microanalysis was applied to determine the chemical compositions of the eutectic phases. The lamellae often point out of the foil edge in the samples. By analysing such regions with a sufficiently narrow electron beam, individual lamellae could be examined. In the JEOL 2000 FX microscope an electron probe of less than 10 nm diameter is easily obtained in the TEM mode.

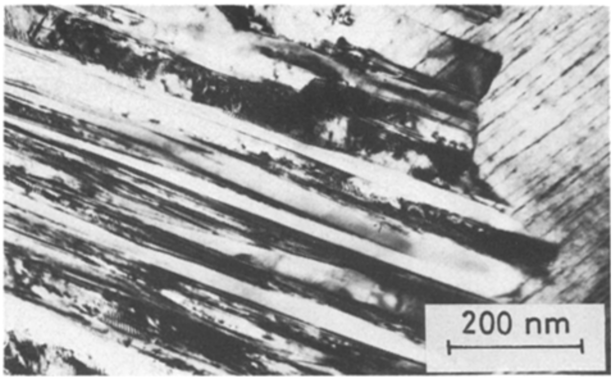

*Figure 1* Eutectic lamellar structure in the as-cast alloy. At the right-hand side is seen the primary phase, containing precipitates parallel to {0 0 1} planes.

The results confirm previous assumptions [2] that there are only two types of lamella, which are alternately enriched in silver and copper, respectively. The silver-rich lamellae are wider than the copper-rich ones. The copper-rich lamellae often appear as the darker, and sometimes display complicated Moiré fringe patterns. Thus the structure may be described as copper-rich plates embedded in a silver-rich matrix. Typical X-ray spectra are shown in Fig. 2.

In Table II the results from the analysis of individual silver-rich lamellae in different eutectic colonies are shown. The mean composition is 50 wt % Au–42 wt% Ag–5.5 wt % Cu–2.5 wt % Pd. In Table III corresponding measurements of copper-rich lamellae are shown. The mean composition is 56 wt % Au–13 wt % Ag–26 wt % Cu–6 wt % Pd. There is a somewhat larger spread in the results from the copper-rich phase. The explanation is that these lamellae are the thinnest and thus the surrounding silver-rich phase might contribute to the analysis in some cases.

In order to determine the mean composition of the eutectic colonies a defocused electron beam was used to cover numerous lamellae. The results thus obtained from different colonies are shown in Table IV. The mean eutectic composition is 53 wt % Au–31 wt % Ag–13 wt % Cu–3 wt % Pd. Using the lever rule and the observed compositions, the weight fraction of the

TABLE II X-ray microanalysis of individual silver-rich lamellae in eutectic colonies (wt %)

| | Au | Ag | Cu | Pd |
|---|---|---|---|---|
| | 52.6 | 39.5 | 7.0 | 0.9 |
| | 49.5 | 42.7 | 5.9 | 2.0 |
| | 46.8 | 43.7 | 5.1 | 4.3 |
| | 47.2 | 43.9 | 5.4 | 3.5 |
| | 50.2 | 43.7 | 4.5 | 1.5 |
| | 50.3 | 41.5 | 5.6 | 2.6 |
| | 50.7 | 39.7 | 6.4 | 3.2 |
| | 49.3 | 41.7 | 6.4 | 2.7 |
| | 52.4 | 38.6 | 6.2 | 2.9 |
| | 48.2 | 43.6 | 4.4 | 3.9 |
| | 49.7 | 45.3 | 3.5 | 1.4 |
| Mean value | 49.7 | 42.2 | 5.5 | 2.6 |
| Standard deviation | 1.8 | 2.1 | 1.0 | 1.0 |

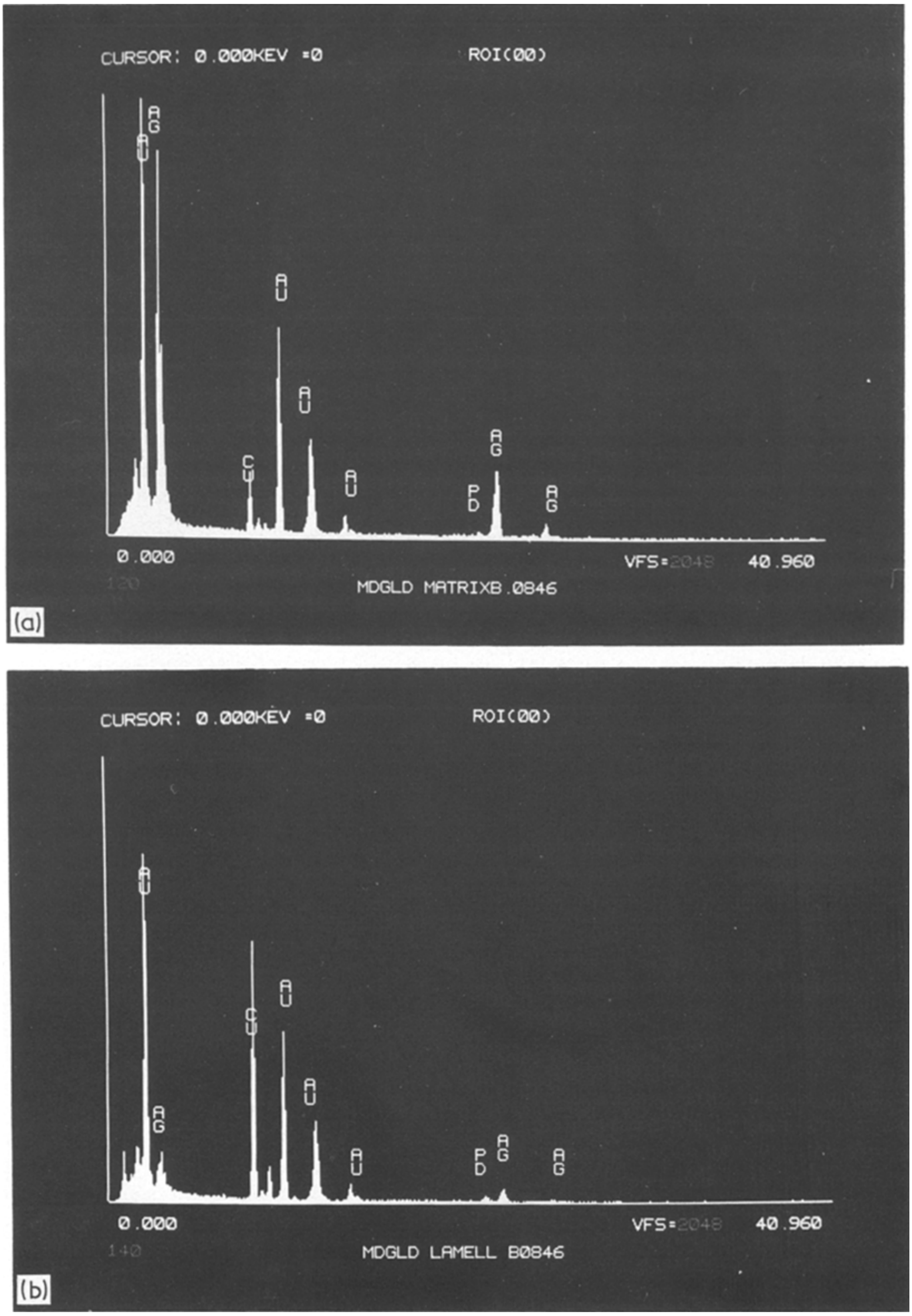

*Figure 2* Typical X-ray spectra obtained from the two types of eutectic lamellae: (a) silver-enriched lamella, (b) copper-enriched lamella.

copper-rich phase in the eutectic was calculated to be about 0.4.

In Fig. 3 the results are illustrated by using the ternary phase diagram for Au–Ag–Cu. In the diagram palladium has been omitted by plotting relative weight fractions of gold, silver and copper. This is equivalent to projecting points in the quaternary Au–Ag–Cu–Pd tetrahedron from the palladium corner on to the Au–Ag–Cu side.

The observed compositions of the eutectic phases are fairly close to the two equilibrium phases formed in this alloy after a long time of annealing [3] at 500° C: 50 wt % Au–(40 to 42) wt % Ag–(1 to 1.5) wt % Pd and 60 wt % Au–28 wt % Cu–2.5 wt % Pd, respectively However, this heat treatment also produced a third, palladium-rich equilibrium phase, which explains the fairly low palladium content in the other two phases.

The segregation behaviour of palladium should be noted since palladium is known to increase the tarnish resistance. During solidification the primary silver-rich phase is somewhat enriched in palladium, while the melt is accordingly depleted. During growth of the eutectic structure the copper-rich phase is enriched in palladium.

The crystallography of the eutectic lamellae was

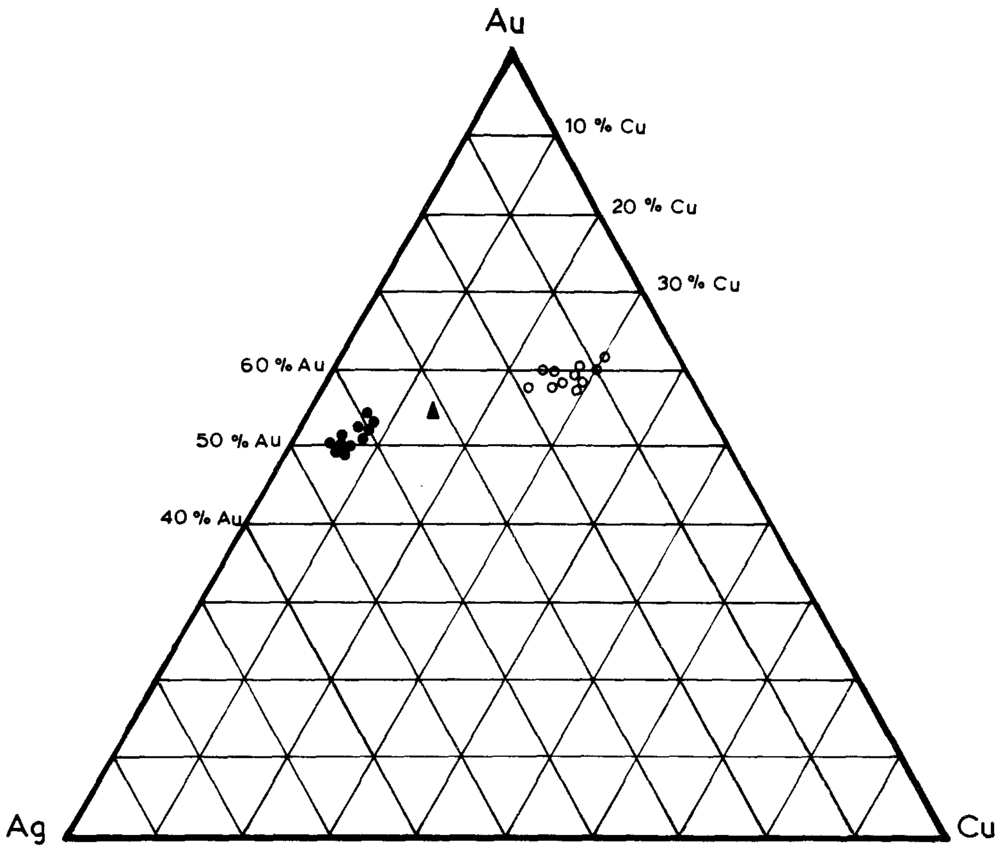

*Figure 3* The observed chemical compositions (wt %) of individual eutectic lamellae, plotted in the ternary Au–Ag–Cu phase diagram (palladium has been omitted). (○) Copper-rich, (●) silver-rich, (▲) mean value.

studied by selected-area diffraction and dark-field microscopy. Part of a eutectic colony is shown in Fig. 4. The corresponding diffraction pattern (Fig. 5) is interpreted as a superposition of the ⟨1 0 0⟩ zone of the fcc silver-enriched matrix and the (*h k* 0) zone of the fct phase AuCu-I. It is seen that only one orientation of the tetragonal phase was present within the selection aperture. More often several orientations are present, however. The same grain-boundary morphology and crystallographic relationship of AuCu-I and a silver-rich phase has also been observed in an alloy after a long heat treatment [5] at 300° C. Within the silver-rich phase in the eutectic structure precipitation in the solid state has taken place, and parallel to {0 0 1} planes one observes fine plate-like precipitates.

TABLE III X-ray microanalysis of individual copper-rich lamellae in eutectic colonies (wt %)

| | Au | Ag | Cu | Pd |
|---|---|---|---|---|
| | 53.3 | 14.8 | 25.2 | 6.8 |
| | 53.6 | 15.6 | 24.0 | 6.8 |
| | 56.2 | 15.5 | 22.2 | 6.1 |
| | 57.8 | 13.8 | 24.2 | 4.2 |
| | 55.5 | 12.6 | 28.7 | 3.2 |
| | 55.7 | 12.0 | 28.0 | 4.3 |
| | 56.1 | 10.1 | 25.2 | 8.6 |
| | 57.8 | 6.3 | 27.0 | 8.9 |
| | 56.5 | 11.7 | 26.1 | 5.7 |
| | 56.6 | 9.8 | 28.6 | 4.9 |
| | 54.2 | 19.2 | 22.4 | 4.1 |
| Mean value | 55.8 | 12.9 | 25.6 | 5.8 |
| Standard deviation | 1.4 | 3.3 | 2.2 | 1.8 |

TABLE IV X-ray microanalysis of eutectic regions (wt %)

| | Au | Ag | Cu | Pd |
|---|---|---|---|---|
| | 52.9 | 31.0 | 12.7 | 3.3 |
| | 52.1 | 30.8 | 13.8 | 3.4 |
| | 53.5 | 30.7 | 13.1 | 2.7 |
| Mean value | 52.8 | 30.8 | 13.2 | 3.1 |

Also the pre-eutectic silver-rich phase, i.e. the matrix, contains a high density of fine precipitates parallel to {0 0 1} planes (Fig. 6a). These fine precipitates have been examined previously and are thought to be the fct phase AuCu-I. In Fig. 6b a dark-field micrograph is shown, recorded by using a $(0\,0\,1)_{\mathrm{AuCu\text{-}I}}$ reflection (Figs 6c and d). The *c*/*a* ratio for the phase is about 0.92.

## 5. Discussion

The accuracy of EDS analysis in transmission electron microscopy depends upon the elements present, the

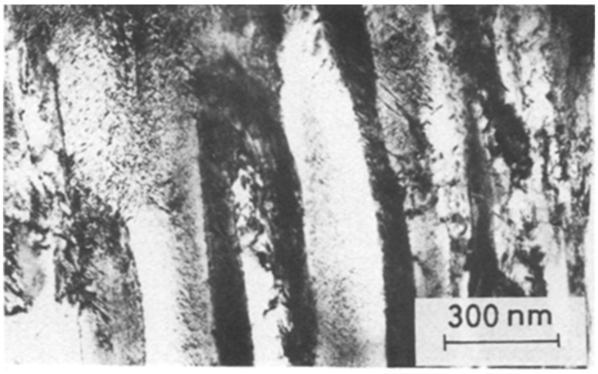

*Figure 4* Eutectic colony chosen for examination by selected-area diffraction (see text). The silver-enriched component (bright regions) has precipitated as thin plate-like particles.

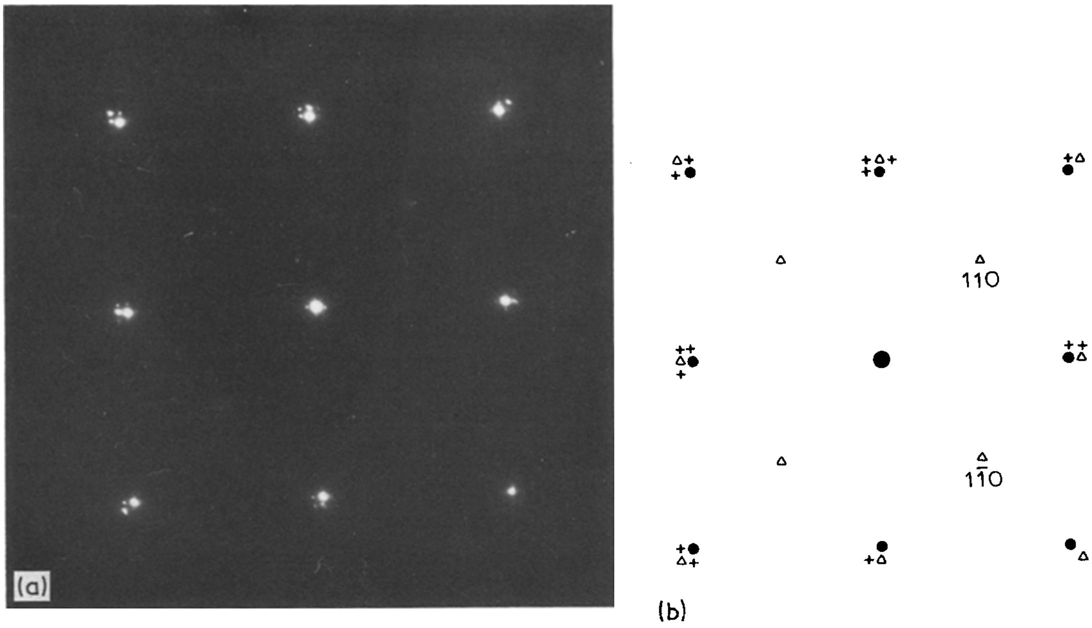

*Figure 5* (a, b) Selected-area diffraction pattern obtained from eutectic region shown in Fig. 4. (●) Silver-rich, (△) copper-rich, (+) double diffracted. The copper-enriched lamellae are mainly the phase AuCu-I. Sometimes local regions have only one orientation with respect to the surrounding fcc lamellae in the eutectic.

spectral lines chosen for analysis and the $k$ factors available. The $k$ factors are often calculated using the computer software accompanying the detector system. Except for an intermediate range of energies, the $k$ factors will depend strongly on the instrumental system. When the foil thickness exceeds a limiting value, corrections for X-ray absorption and fluorescence will be necessary. With the higher primary voltages available in electron microscopy, high-energy X-ray lines can be used in the analysis. There is less need for absorption corrections when high-energy X-ray lines are used. The thin-film criterion quoted by Goldstein [7] is

$$(\chi_A - \chi_B)\varrho t/2 < 0.1 \tag{2}$$

$\chi$ is equal to $\mu \operatorname{cosec} \alpha$, where $\mu$ is the mass absorption coefficient for the X-ray line in the foil, $\alpha$ is the take-off angle, $\varrho$ the density and $t$ the thickness of the foil. In the present study the $L\alpha$ line for gold instead of the $M\alpha$ line was used, and also the $K\alpha$ lines for silver and palladium instead of the $L\alpha$ lines.

By using Criterion 2 the limiting thickness is 100 nm if Au$M\alpha$ and Cu$K\alpha$ are used. If the Au$L\alpha$ line is used instead, this limit is raised to the order of one micrometre. In the current investigation, absorption corrections, based on tedious thickness determination of the individual lamellae, could therefore be avoided.

The compositions of eutectic lamellae are expected to represent those of a quasi-binary eutectic. If palladium is neglected, the compositions determine a tie-line in the ternary phase diagram (Fig. 3). Although the microstructure of the cast alloy is quite complex, its broad features may be discussed in terms of the binary systems formed by the three main components: copper has limited solid solubility in silver, whereas both copper and silver form continuous solid solutions with gold. In the Au–Cu system there is a tendency to form ordered structures, the tetragonal AuCu–I phase being most likely to occur in the present gold-rich system.

The fine precipitates formed in the pre-eutectic silver-rich matrix during cooling have been discussed

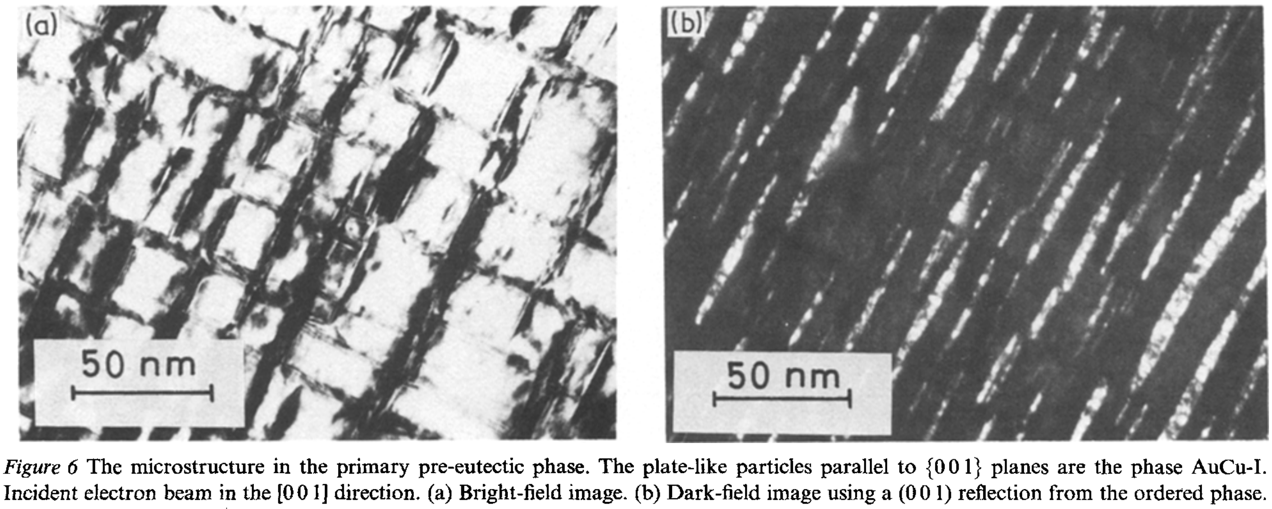

*Figure 6* The microstructure in the primary pre-eutectic phase. The plate-like particles parallel to {001} planes are the phase AuCu-I. Incident electron beam in the [001] direction. (a) Bright-field image. (b) Dark-field image using a (001) reflection from the ordered phase. (c, d) Corresponding selected-area diffraction pattern. The platelets viewed "edge-on" in (a) correspond to the two orientations A and B.

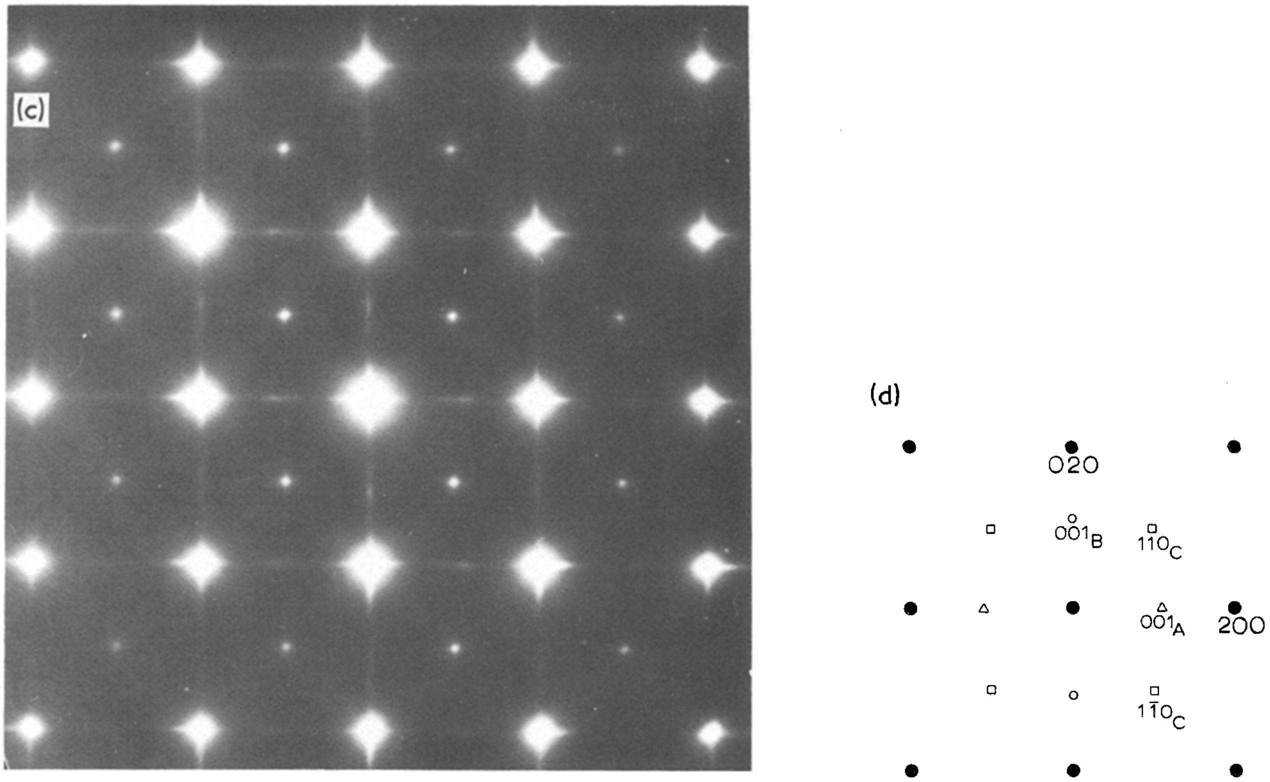

*Figure 6* Continued.

previously [2]. The diffraction patterns and dark-field pictures (Fig. 6) identify these precipitates as copper-rich thin platelets on $\{1\,0\,0\}$ planes with the *c* axis of the tetragonal AuCu-I perpendicular to the platelet plane. The $c/a$ ratio of 0.92 is close to what is found in alloys near 50:50 at % composition. The AuCu-I phase has been observed previously by X-ray diffraction in the ternary alloy Au–Ag–Cu in a region adjacent to its stochiometric composition in the binary Au–Cu diagram [8]. Presumably these plates are initiated by a spinodal decomposition, followed by coarsening and eventually formation of the fct ordered phase. Hence they may not have reached the equilibrium composition, but may contain less copper than the copper-rich component of the eutectic.

Within the silver-rich phase in the eutectic structure there is also evidence of precipitation during cooling of the solid. The observations indicate that the silver-rich eutectic component contains precipitates with a morphology similar to the matrix, but on a finer scale (Fig. 4). The copper-rich eutectic lamellae produced a more complicated picture. Although observations are few, it seems likely that the copper-rich lamellae are the phase AuCu-I, sometimes with only one crystallographic orientation to the embedding silver-rich phase. Dark-field micrographs from superstructure reflections revealed no plate-like morphology within the lamellae characteristic of a tetragonal phase, and the diffraction patterns indicate that the $c/a$ ratio is much closer to unity than for the AuCu-I platelets in the pre-eutectic matrix. This is in accordance with the quite high copper content in these lamellae, which corresponds to a Cu/Au atomic ratio of 3/2. The fringe contrast seen within the copper-rich lamellae (Figs 1 and 4), with a spacing of about 3 nm, was not observed in dark-field pictures. The contrast is presumably due to a Moiré effect, possibly between overlapping silver-rich and copper-rich lamellae. This seems to be supported by the extra spots in the diffraction pattern which can be attributed to double scattering involving both the silver-rich and copper-rich lamellae.

## 6. Conclusions

The compositions of the eutectic lamellae were found to be 56 wt % Au–13 wt % Ag–26 wt % Cu–6 wt % Pd and 50 wt % Au–42 wt % Ag–5.5 wt % Cu–2.5 wt % Pd. This corresponds well with a mean eutectic composition of 53 wt % Au–31 wt % Ag–13 wt % Cu–3 wt % Pd. The weight fraction of the copper-rich phase was 0.4.

The Ag$K\alpha$ and Au$L\alpha$ lines were used for the EDS analysis. Thus absorption corrections were unnecessary at the accuracy level sought. The *k* factors had to be determined experimentally, however.

Plate-like precipitates inside the pre-eutectic matrix as well as inside the silver-rich phase in the eutectic were found to be of tetragonal AuCu-I type. Ordering within the copper-rich lamellae in the eutectic produced a complicated microstructure. Palladium has previously been found to be enriched in the pre-eutectic silver-rich matrix. In the eutectic solidification, palladium follows copper, however.

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