ELEMENT DISTRIBUTION IN GOLD-PLATINUM ALLOYS

A PILOT STUDY WITH THE ELECTRON MICRO-PROBE

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Studies of the homogeneity of gold alloys have usually relied upon microscopic examination of the polished, etched surface of the alloy, and it has been assumed that the absence of dendrites in the microscopic picture indicates that the alloy is homogeneous, or practically so. Small departures from homogeneity cannot, however, be detected by this method. It is limited to carat-gold alloys and certain other relatively large-grained alloys; many of the platinum-gold alloys display no dendrites after casting. Nevertheless, from purely theoretical considerations it can be assumed that they are not homogeneous.

Attempts to find another method for examining the homogeneity of these alloys have been made by, among others, *Björn & Wennström* (1962). With the publication by *Björn* in 1962 of some tests with an electron micro-probe arranged for point analysis it was evident that a method had been found that promised to be of value in research of element distribution in platinum-gold alloys. The encouraging results prompted further experiments, the method being extended to include linear analysis and preparation of scanning pictures showing the distribution of alloy components in a given surface.

The present paper gives an account of pilot experiments primarily on line analysis of two platinum-gold alloys after casting and heat treatment.

THE ELECTRON MICRO-PROBE

Studies with the electron micro-probe are based on analysis of the X-radiation emitted from a material bombarded by high-energy electrons. The source of electrons is a heated tungsten filament in the instrument itself, in which a high vacuum is maintained. By electromagnetic coils the electron stream can be focused to a beam less than 0.001 mm in diameter. Since the electrons are rapidly retarded by the material under examination the analysis will presumably not involve a volume of more than a few cubic microns.

As mentioned above, the specimen will emit X-radiation the wavelength of which is characteristic of each constituent element and the intensity of which is approximately proportional to the percentage of the respective elements present. The various wavelengths are analysed by a crystal that reflects the characteristic radiation to a detector. This measures the radiation intensity. For quantitative analysis comparative measurements are made of the intensity from the sample and a body of known composition, usually the pure element.

The linear scanning of the surface of a sample to examine the distribution of the element along the line is performed with a special addition to the instrument. The specimen is mounted in a holder which is moved automatically in the required direction, and the recording instrument (oscilloscope or automatic writer) is synchronized with this movement. With a recorder having several channels a linear analysis of several components of an alloy can be performed simultaneously. This was the method used in this study.

The scanning can also be performed in any required parallel pattern so that a selected area of the specimen can be examined. The intensity of the oscilloscope beam is modulated by the recorded intensity of the X-rays, and photographs are taken of the image on the screen. From such a scanning picture any departure from uniformity of distribution of a component may be detected. This method, too, was tried out in the present study.

MATERIAL

Two gold-platinum alloys were chosen. Both consisted chiefly of gold, silver, copper and zinc; alloy 1 also contained platinum

and palladium (about 3 per cent of each) whereas alloy 2 contained about 10 per cent of platinum.

PREPARATION AND TREATMENT OF THE SPECIMENS

For the experiments rods 7 mm long and 4 mm in diameter were made from each of the alloys by the dental casting method. The alloys were melted with a gas flame in the usual way. The casting ring was heated to 525° before casting. After the button had ceased to glow, the casting ring was rapidly cooled.

From each alloy sample two slices were sawn, one for analysis of the distribution of the alloy components resulting from the dental casting method, and the other for analysis after heating in an electric oven at 800° C for 30 minutes.

The cast and heat-treated specimens were imbedded in bakelite in the normal way, ground and polished, etched slightly in aqua regia and placed in the instrument for examination — chiefly by linear analysis. For this purpose 2 or 3 grains in the centre of the specimen were used. For obvious reasons the cut was directed so as to pass through the centre of the largest grain cross-section.

RESULTS

The results of the linear analyses of the cast and heat-treated specimens are presented in figures 1 and 2. The mean concentration of each constituent of the alloys is set at zero. The variations from the mean composition are also marked. The vertical lines (B) denote the grain boundaries.

For most of the constituent elements there were considerable differences in distribution between the boundary and the centre of the grain. In the case of alloy 1, for instance, there was a considerably larger proportion of platinum in the interior than at the boundary. For gold and copper the opposite was the case, while silver and zinc appeared to be fairly uniformly distributed.

The heat treatment, which was performed to equalize the distribution, was largely effective. At the treatment for alloy 1 the inequalities in the concentration of copper and probably also of gold were completely removed (Fig. 1); there was some equilibration also for platinum; for silver there was no difference after

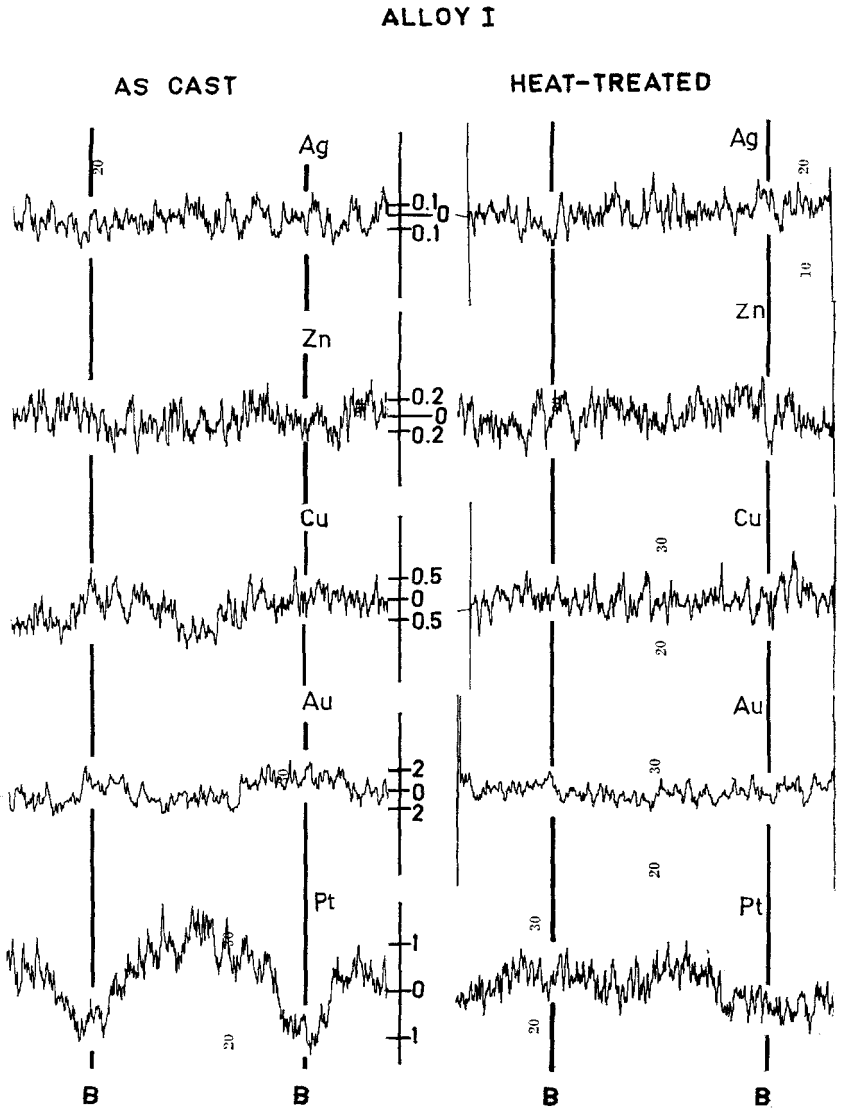

Fig. 1. Variation in distribution of the elements in Alloy 1 (with the exception of Pd) as revealed by the electron micro-probe. To the left: alloys as cast; to the right: alloy specimen heat-treated at 800°C for 30 minutes. B = grain boundary.

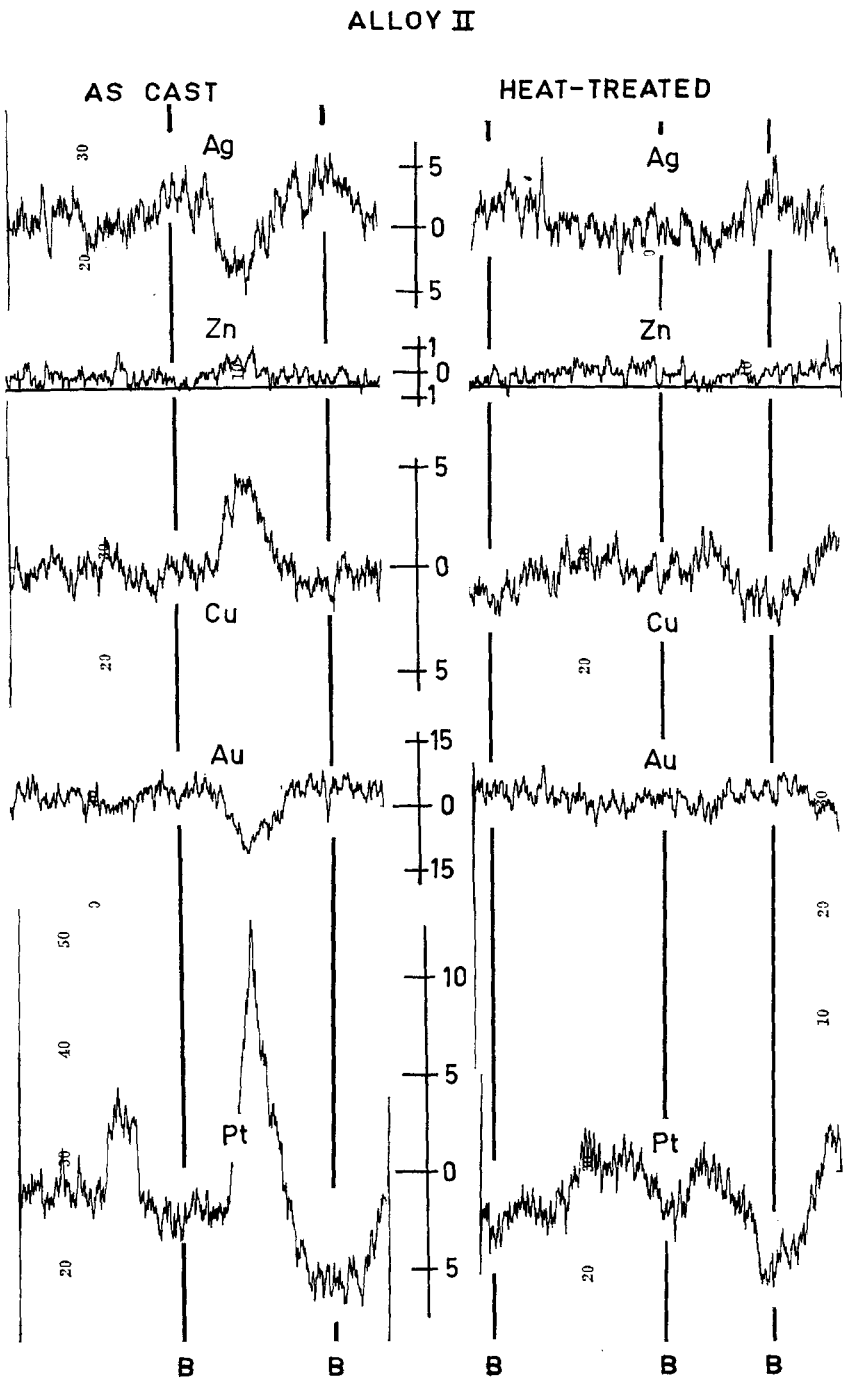

Fig. 2. Variation in distribution of the elements in Alloy 2 as obtained through the electron micro-probe. To the left: alloy as cast. To the right: alloy specimen heat-treated at 800° C for 30 minutes. B = grain boundary.

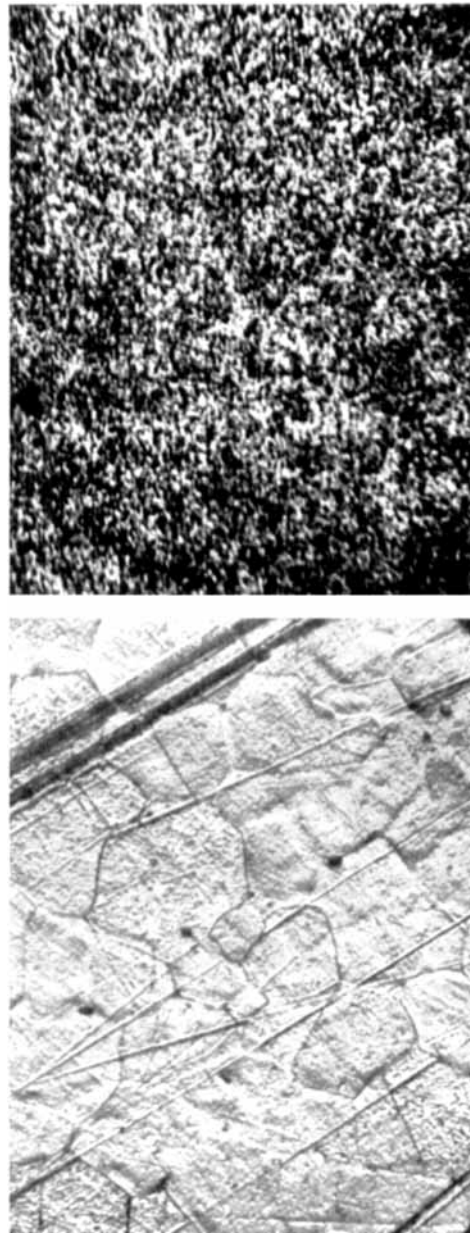

Fig. 3. Alloy 1 as cast. Etched optical picture (below) and scanning picture (above) obtained with the electron micro-probe showing the uneven Pt-distribution within the same surface.

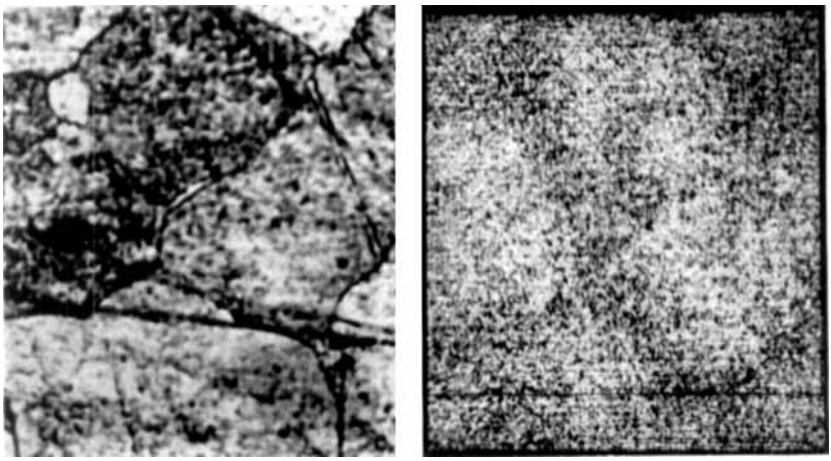

Fig. 4. Alloy 2 as cast. Etched optical picture to the left. Scanning picture to the right obtained with the electron micro-probe showing Pt-distribution within the same surface. At the grain boundaries the Pt-concentration is obviously lower than in the interior of the grain.

treatment, this being evenly distributed here, too. On the other hand zinc, which after casting was evenly distributed within the grain, tended to migrate towards the boundary during heating.

In alloy 2 for the platinum the observations after casting only, were the same but the difference was considerably more pronounced than for alloy 1. Copper was also found mainly in the centre, but the highest concentration of silver and gold was at the boundary. As regards zinc the distribution was fairly uniform (Fig. 2).

Heat treatment of the alloy 2 (Fig. 2) produced no definite change in distribution of zinc, though, in some measure, in that of copper. For silver the difference in concentration at the boundary and in the interior was smoothed out, to a marked extent, though not completely. The same applies to platinum where, however, there was initially a high concentration in the centre. For gold, too, there was a definite levelling out of the concentration.

The initial distribution of platinum was confirmed by the scanning picture (Figs. 3 and 4). From a comparison of the etched optical picture and the scanning picture it is evident that

this metal was highly concentrated in the interior of the grain. This was particularly clear for alloy 2, with its comparatively high content of platinum.

DISCUSSION

In studies of the segregation in dental castings *Souder & Paffenbarger* (1942) have shown that the alloy constituents were present in the same proportion throughout a particular casting; this suggests that there is no intercrystalline segregation. As regards our results, there is reason to suppose that the two saw slices in the specimens of the present study were equivalent.

The results of these pilot experiments strongly indicate that intracrystalline segregation occurs in casting by the dental method also with dental alloys containing platinum in a gold, copper and silver base.

As might be inferred from theoretical considerations, the alloy components with a high melting point seem to be concentrated in the centre parts of the individual grain, while those with a low melting point are concentrated more at the periphery of the grain. The results for alloy 2 provide a striking illustration of this.

For alloy 1 the same probably applies, in spite of the fact that for copper the concentration at the periphery was higher than in alloy 2. Alloy 1 also contained palladium, with a melting point considerably higher than that of copper (1555° against 1083° C), so that there is reason to suppose that, together with platinum, it has a higher concentration in the interior of the grain and forces the copper out to the periphery on solidification. The role of palladium in dental alloys calls for further study.

The heat treatment resulted in a definite levelling out of the differences in concentration for all the components with the possible exception of zinc.

The variation from the mean composition for silver was comparatively small and the reduction of the concentration on heating therefore took place fairly rapidly. The same applies to gold, whereas copper appears to be slightly more sluggish.

Since the diffusion rate is lower for platinum than for the other components, the levelling out of the concentration of this

constituent in both alloys as a result of the heating procedure will be fairly restricted. In alloy 1, with the lower platinum content, the diffusion was apparently more rapid. On the other hand, there is some difference between the two alloys even as cast. That palladium can be responsible for this is a possibility that calls for examination.

It is clear from the results that after casting of platinum-gold alloys there is intracrystalline segregation, which is not necessarily visible under the microscope. It would be rewarding to study further the segregation also in carat gold alloys using different techniques of heat treatment.

The present method would seem to be suitable for examining the concentration of dental alloys subjected to different treatment conditions. It would seem to be a useful complement to the microscopic and X-ray crystallographic methods and promises to deepen our understanding of the structure of dental alloys.

SUMMARY

The present paper gives an account of pilot experiments primarily on line analysis of two platinum-gold alloys, with and without heat-treatment, using the electron micro-probe to obtain information on the distribution of alloy components in a given surface. The gold-platinum alloys consisted chiefly of gold, silver, copper and zinc; alloy 1 also contained platinum and palladium (about 3 per cent of each) whereas alloy 2 contained about 10 per cent of platinum.

The cast and the heat-treated specimens of the alloys were inbedded, ground and polished, etched slightly and placed in the instrument for examination by linear and scanning analysis. For this purpose the grains in the centre of the specimen were used.

The results of the linear analyses of the specimens are presented in figures 1 and 2. It is clear from the results that after casting of platinum-gold alloys there is intra-crystalline segregation, which is not necessarily visible under the microscope. The alloy components with a high melting point are concentrated in the centre of the individual grain, while those with a low melting point are concentrated more at the periphery. The

heat-treatment resulted in a definite levelling out of the differences in concentration for all the components.

Line and scanning analysis with the electron micro-probe appears to be suitable for future studies on concentration and distribution of alloy components in dental alloys.

RÉSUMÉ

DISTRIBUTION DES CONSTITUANTS DANS LES ALLIAGES OR-PLATINE

Le présent article rend compte d'expériences préliminaires concernant essentiellement une analyse linéaire de deux alliages or-platine, avec et sans traitement thermique, en utilisant la microsonde électronique pour obtenir des renseignements sur la répartition des constituants de l'alliage dans une surface donnée. Les *alliages or-platine étaient principalement constitués d'or*, d'argent, de cuivre et de zinc; l'alliage 1 contenait de plus du platine et du palladium (environ 3 % de chaque) tandis que l'alliage 2 contenait environ 10 % de platine.

Les spécimens d'alliage coulés et ceux ayant subi un traitement thermique ont été enrobés, meulés et polis, attaqués légèrement à l'acide et placés dans l'instrument pour l'examen par analyse linéaire et par balayage. A cet effet, les grains du centre des spécimens ont été utilisés.

Les résultats des analyses linéaires des spécimens sont présentés sur les figures 1 et 2. Il ressort clairement de ces résultats qu'après la coulée des alliages or-platine, il y a ségrégation intracristalline, ce qui n'est pas nécessairement visible au microscope. Les constituants de l'alliage qui présentent un point de fusion élevé sont concentrés au centre de chaque grain, tandis que ceux qui possèdent un point de fusion bas sont concentrés plutôt à la périphérie. Le traitement thermique a résulté, pour tous les constituants, en un nivellement net des différences de concentration.

Les analyses linéaire et par balayage au moyen de la microsonde électronique paraissent convenir pour les études à venir sur la concentration et la distribution des constituants des alliages dans les alliages pour usage dentaire.

ZUSAMMENFASSUNG

VERTEILUNG VON LEGIERUNGSKOMPONENTEN IN GOLDPLATIN-LEGIERUNGEN

Dieser Artikel beschreibt einige orientierende Versuche, die Verteilung von Legierungskomponenten in zwei Goldplatinlegierungen mit Hilfe einer Elektron-Mikrosonde festzustellen. Die untersuchten Legierungen enthielten Gold, Silber, Kupfer und Zink als Basiskomponenten sowie ungefähr 3 % Platin und Palladium in der einen Legierung und ungefähr 10 % Platin in der anderen. Die Untersuchungen wurden an gegossenen Probekörpern sowie an gegossenen und wärmebehandelten Probekörpern ausgeführt. Die Wärmebehandlung wurde während 30 Minuten bei einer Temperatur von 800° C vorgenommen.

Die gegossenen und die wärmebehandelten Probekörper wurden in Bakelit eingebettet, geschliffen und poliert sowie leicht geätzt, wonach sie in das Instrument für eine Linienanalyse sowie für eine "Scanning"-Analyse eingesetzt wurden. Für diese Analyse wurden Kristalliten (Korn) im Zentrum des Probekörpers benutzt.

Die Resultate der Linienanalyse werden in Abb. 1 und 2 vorgeführt. Aus diesen geht klar hervor, dass eine intrakristalline Seigerung in den Güssen von Goldplatinlegierungen auftritt, obgleich diese Seigerung im gewöhnlichen Metallmikroskop nicht sichtlich ist. Die Legierungsbestandteile, die die höchste Schmelztemperatur haben, haben eine höhere Konzentration im Kornzentrum, während die mit niedrigerer Schmelztemperatur mehr in der Kornperipherie konzentriert werden. Wärmebehandlung gab einen deutlichen Konzentrationsausgleich für die in den Legierungen enthaltenen Bestandteile, möglicherweise mit Ausnahme für Zink.

Linienanalyse und "Scanning"-Analyse mit Hilfe einer Elektron-Mikrosonde scheint eine geeignete Methode für Studien über Probleme hinsichtlich der Elementverteilung in dentalen Legierungen zu sein.

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