# Grain-refined Recrystallized 14-Carat Gold Alloy
## EFFECT OF SMALL ADDITIONS OF ELEMENTS IN AN AU-AG-CU-ZN ALLOY

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*Prevention of excessive grain growth during annealing treatments is important for jewellery applications of gold alloys. The beneficial effects of small amounts of a number of metals of high melting points and low solubilities in gold to dental gold alloys are well known. Some of these elements, and others, have been added singly or in combinations, to a 14-carat gold jewellery alloy and their effects on grain size, on recrystallization, and on the formation of 'orange peel' during subsequent cold working have been studied. Possible mechanisms by which grain refining during solidification and annealing is brought about by small additions of certain elements are discussed in the light of the data obtained.*

The process of jewellery fabrication by cold working inevitably involves intermediate annealings the purpose of which is to restore alloy ductility by recrystallization of the work-hardened structure. The annealing treatments, however, can lead to coarse-grained structures as a result of excessive grain growth during recrystallization. Due to the fact that plastic flow in crystals is orientation-dependent, on further deformation, especially if operations such as deep drawing or bending are involved, such structures can manifest themselves undesirably by producing a surface effect known as 'orange peel'.

In the practice of jewellery fabrication it is not always possible to prevent the appearance of 'orange peel' by strict control of annealing parameters. It is therefore desirable to develop jewellery alloys resistant to excessive grain growth in a wide range of annealing conditions. In principle, this can be achieved by introducing small amounts of certain elements which restrict the rate of grain growth during annealing without affecting significantly other alloy properties (1).

It is now a well established fact that, added in very small amounts, some metals with high melting points and low solubility in gold produce grain refinement of the cast structure in gold (2) and in some gold alloys (3). Because of this effect 0.01 to 0.1 per cent iridium, ruthenium or rhenium are included in compositions of most dental alloys patented during the last two decades.

Far less is known about the influence of small additions on the grain size of jewellery alloys. Positive effects of 0.005 to 0.05 per cent iridium, ruthenium and rhenium on white nickel-containing alloys (4) and 1 per cent rhodium on gold alloys containing 30 to 50 per cent platinum (5) have been reported. In yellow jewellery alloys grain refining by 0.01 to 0.1 per cent iridium (introduced together with 0.2 to 0.5 per cent cobalt), (6), 0.2 per cent ruthenium or osmium (7), and small additions of nickel and cobalt (8) has been claimed. Recently, a comprehensive study has been made of the effects of small additions of more than 20 elements and some combinations of them on various properties, including grain size

of solidified and recrystallized structures, of gold (9), 18 carat gold-copper (10) and gold/12.5 silver/12.5 copper per cent (11) alloys. More than a hundred compositions were investigated. As could be expected, 0.025 and 0.1 per cent iridium, 0.1 per cent ruthenium and 0.3 per cent rhodium produced grain refinement of solidified structures of both alloys (their effect on gold was not tested). Grain refinement of the cast structure of the ternary alloy was also achieved by additions of 0.1 and 0.5 per cent vanadium, 0.1 per cent lead and 0.1 per cent bismuth. Small additions of barium, zirconium, niobium and tantalum to pure gold showed definite grain refinement of its cast structure, the effect being retained after cold working and annealing at 600 °C for 1h. In the case of annealed structures, combinations of cobalt and barium, cobalt and molybdenum, and nickel with molybdenum when added to pure gold all gave strong grain refinement whereas individual additions of cobalt, nickel and molybdenum showed slight or no effect.

In the binary alloy, annealed for 1h at 700 °C after 70 per cent deformation, substantial grain refining was achieved with small additions of iridium, cobalt and manganese + barium. Additions of rhenium and rhodium to the gold-copper alloys gave only moderate grain refinement in the case of annealed structures. A wider range of additions had a grain refining effect on the ternary alloy — probably because this alloy showed 50 per cent larger grain size than the binary one after the same annealing treatment. Grain refining was strong with additions of iridium, zirconium and barium, all at the 0.1 per cent level, 0.5 per cent vanadium, 0.02 per cent lead and 0.025 per cent bismuth. Moderate refining of the grain size was achieved by selected additions of ruthenium, rhodium, nickel, cobalt, titanium, tin, silicon, combinations of cobalt + ruthenium and nickel + molybdenum. The only information available on grain refining in 14-carat gold alloys is that an addition of 0.2 per cent cobalt to a gold/30 silver/11.5 copper per cent alloy gives a fine-grained cast structure that is retained after cold working and annealing, and prevents the formation of the 'orange peel' pattern on subsequent cold working (1).

It should be noted that some of the effective grain refining additions mentioned above cannot be used for practical purposes in jewellery alloys. For example, the very high reactivity of barium makes it difficult to control its concentration in the alloy during scrap remelting, and elements such as lead, bismuth, antimony and tin that are insoluble in gold and form low-melting eutectic layers on grain boundaries have a detrimental effect on the mechanical properties of the alloys. It should be also mentioned that at certain concentrations some additions, in particular those of chromium and iron, can cause a marked coarsening of the annealed structure (12).

The purpose of the research reported below was to find an element or a combination of elements which, when added to a 14-carat gold-silver-copper alloy containing 6 per cent zinc, would act as an effective grain refiner of its recrystallized structure over a wide range of annealing temperatures and, if possible, also act as a refiner of its cast structure.

## Experimental

In the first stage of the investigation additions of five elements were introduced separately to the gold alloy in the following concentrations (weight per cent):

Ir  0.02, 0.05
Zr  0.04, 0.05, 0.1
Co  0.05, 0.1, 0.15, 0.2, 0.3
B  0.005, 0.01, 0.1
Y  0.02

The choice of iridium, zirconium and cobalt was based on data contained in the literature reviewed above; these elements seemed the most effective grain refiners in the groups of elements to which they belong. the effect of the two other elements — boron and yttrium — on gold alloys has not yet been studied, but they have been reported (13, 14, 15) to produce grain refinement of the structures of both annealed and cast copper and copper alloys.

In the second stage, gold alloys with additions of the following combinations of elements (weight per cent) were investigated:

0.1 Zr + 0.005 B
0.15 Co + 0.005 B
0.1 Co + 0.05 Zr + 0.005 B
0.1 Co + 0.1 Ni + 0.05 Zr + 0.005 B

Alloys were prepared by induction melting in a graphite crucible under argon protection and poured into a steel mould. The ingots had a diameter of 6 mm and a mass of about 42 g. Some alloys were also prepared as 250 g ingots of 9x9 mm cross-section by induction melting under protection of a hydrogen flame.

Solidification structures were investigated using samples cut from both the bottom and top sections of the ingots. The rest of the ingot was cold worked into wire 1 mm in diameter with intermediate annealing at 680 °C. Although it had been found that the annealed grain size did not depend on the extent of prior cold working in the range of 5 to 75 per cent, the reduction during the last stage of drawing was kept at 75 per cent for all alloys. The final annealing treatment preceding determination of recrystallized grain size was performed at 600, 680, 700 and 750 °C at various time intervals from 0.5 min to 2 h. The samples were quenched in water from the annealing temperature. Etching in 5 per cent ammonium sulphate + 5 per cent potassium cyanide aqueous solution was carried out prior to metallographic observations.

## Effect of Small Additions on Alloy Structure

Ingots of the unmodified 14-carat gold-silver-copper-zinc alloy showed a well pronounced dendritic segregation (Figure 1 (a)) with dendritic branches being coarser in the upper part of the ingots. The porosity of the ingots was also coarser in the top part. In order to reveal the grain boundaries of the cast microstructure distinctly homogenization annealing was performed (Figure 1 (b)). The average grain size was about 1 mm in the 250 g ingots and 0.3 mm in the 42 g ingots.

The grain size of the annealed microstructure depended drastically on annealing time and temperature. For example, the rise of annealing temperature from 600 to 750 °C resulted in a 20-fold increase of average grain size after 15 min annealing*. No

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* It should be noted that 750 °C is to be considered a very high annealing temperature for the alloy because of its relatively low solidus temperature.

**Table I**

**Effect of Alloying Additions on the Grain Size of the Recrystallized Structure of the Gold Alloy After 15 min Annealing at Various Temperatures**

| Addition, wt. % | Grain size, μm average (min-max) | | | | |
|---|---|---|---|---|---|
| | 600 °C | 650 °C | 680 °C | 700 °C | 750 °C |
| None | 13(6–30) | 35(17–60) | 40(25–100) | 60(25–200) | 170(70–280) |
| 0.1 Zr | 6(3–25) | 30(7–50) | 35(10–60) | 50(17–80) | 80(30–200) |
| 0.1 Zr + 0.005 B* | 15(6–30) | 17(7–35) | 20(10–35) | 25(10–50) | 30(20–100) |
| 0.15 Co + 0.005 B* | 3(1–10) | 3(1–10) | 3(1–10) | 5(1–20) | 20(3–50) |
| 0.1 Co + 0.1 Ni + 0.05 Zr + 0.005 B | 3(1–8) | 3(1–10) | 10(1–30) | 15(5–40) | 20(5–50) |
| 0.05 Ir | 7(3–20) | 10(3–30) | 15(3–40) | 20(5–50) | 25(5–60) |

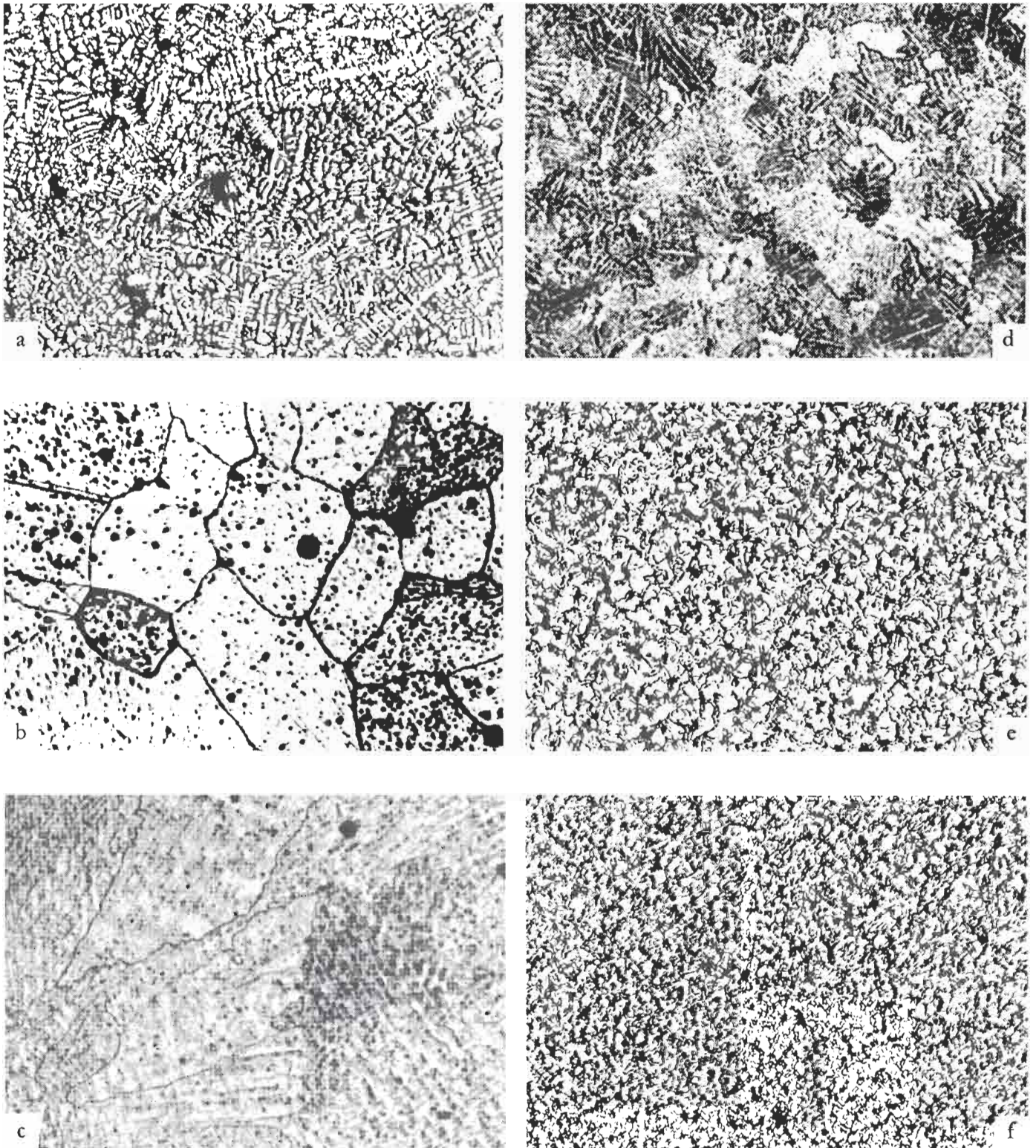*Data for the melt where the most pronounced effect of the addition on grain size was observed

Fig. 1   Effect of small additions of selected elements on the as-cast microstructure of a 14-carat Au-Ag-Cu-Zn alloy: (a) unmodified alloy; (b) as (a), after homogenization annealing, 780 °C, 1 h; (c) addition of 0.01% Zr; (d) addition of 0.15% Co and 0.005% B; (e) addition of 0.05% Ir; (f) as (e), remelted three times

difference, however, was observed in the microstructure of wires prepared from 40 and 250 g ingots in spite of the difference in their as-cast grain sizes.

Boron, yttrium and cobalt introduced separately had no grain refining effect on either the cast or annealed structure of the alloy. Ingots with 0.1 per cent boron had a higher degree of gaseous porosity as indicated by spherical pores up to 1 mm in diameter. A slight increase in grain size was observed in alloys containing yttrium and cobalt after annealing at 700 and 750 °C. Zirconium brought about some changes in the as-cast structure, namely, thinner dendritic branches and more pronounced etching of grain boundaries, but did not affect the grain size (Figure 1 (c)). Zirconium had a slight grain refining effect on the recrystallized structure that was more marked with larger additions (Table I).

Cobalt and zirconium are much more effective when introduced in combination with boron. The gold alloy with 0.1 per cent

zirconium and 0.005 per cent boron has a solidification structure similar to the one presented in Figure 1 (c), but showed further decrease of the recrystallized grain size especially at higher temperatures (Table I). However, at 750 °C sharp variations in grain size are observed as in the case of single zirconium additions. Sharp decrease in grain size of the cast structure (Figure 1 (d)) and a very fine-grained recrystallized structure (Table I) were observed in the alloy containing 0.15 per cent cobalt and 0.005 per cent boron. Unfortunately, this effect was not reproduced in subsequent melts where the cast structure was similar to that of Figure 1 (c) and the recrystallized structure was not finer than that produced by the combined zirconium + boron addition.

A quaternary addition of 0.1 cobalt + 0.1 nickel + 0.05 zirconium + 0.005 boron per cent had a strong and reproducible grain refining effect on the recrystallized structure at all annealing temperatures (Figure 2 (c), Table I). Again, the cast structure
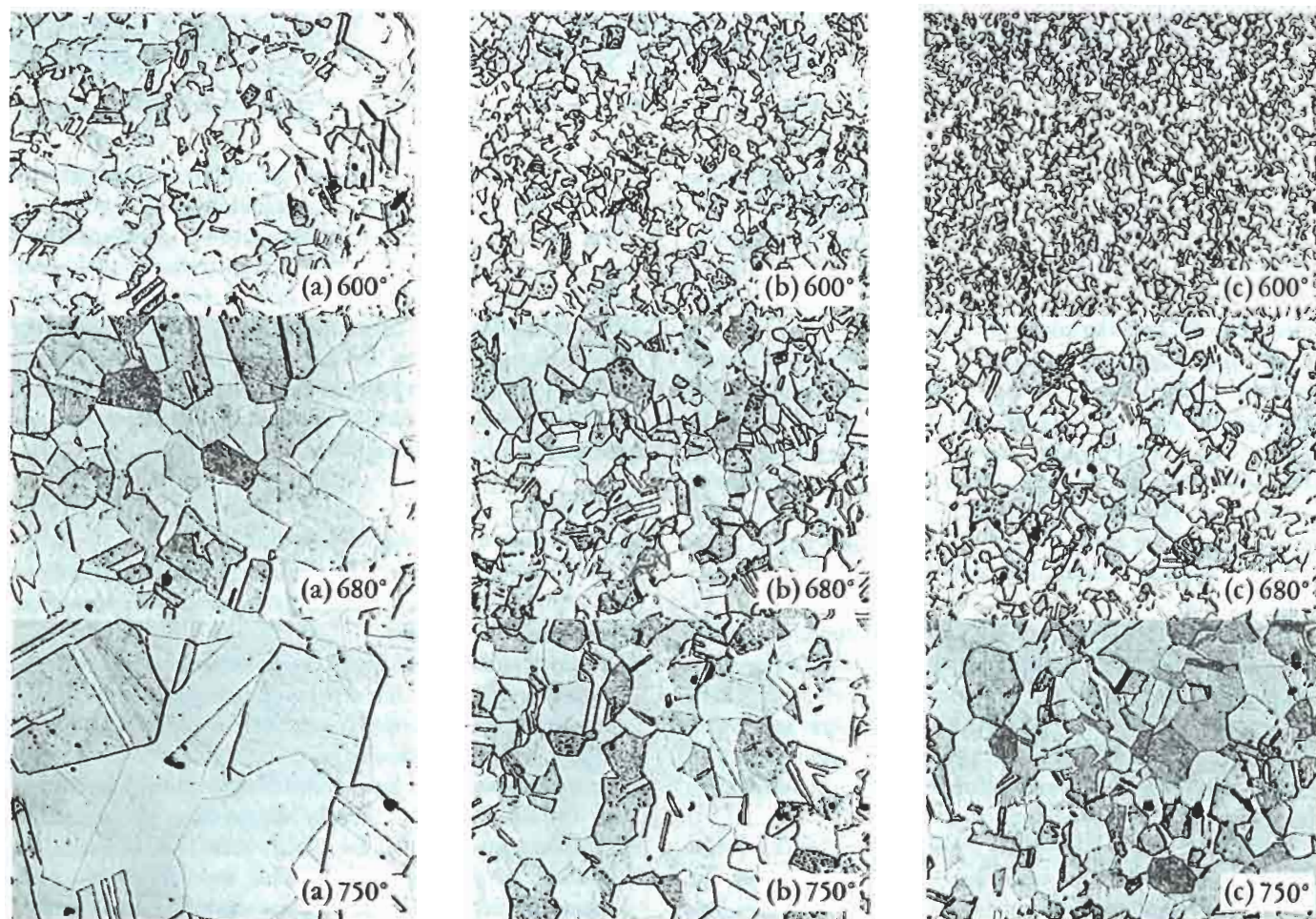


Fig. 2    Effect of small additions of selected elements on the crystallized structure of a 14-carat Au-Ag-Cu-Zn alloy annealed for 15 min at 600 °C (upper row), 680 °C (middle row) and 750 °C (lower row): (a) unmodified alloy; (b) addition of 0.05% Ir; (c) addition of 0.1% Co, 0.1% Ni, 0.05% Zr and 0.005% B
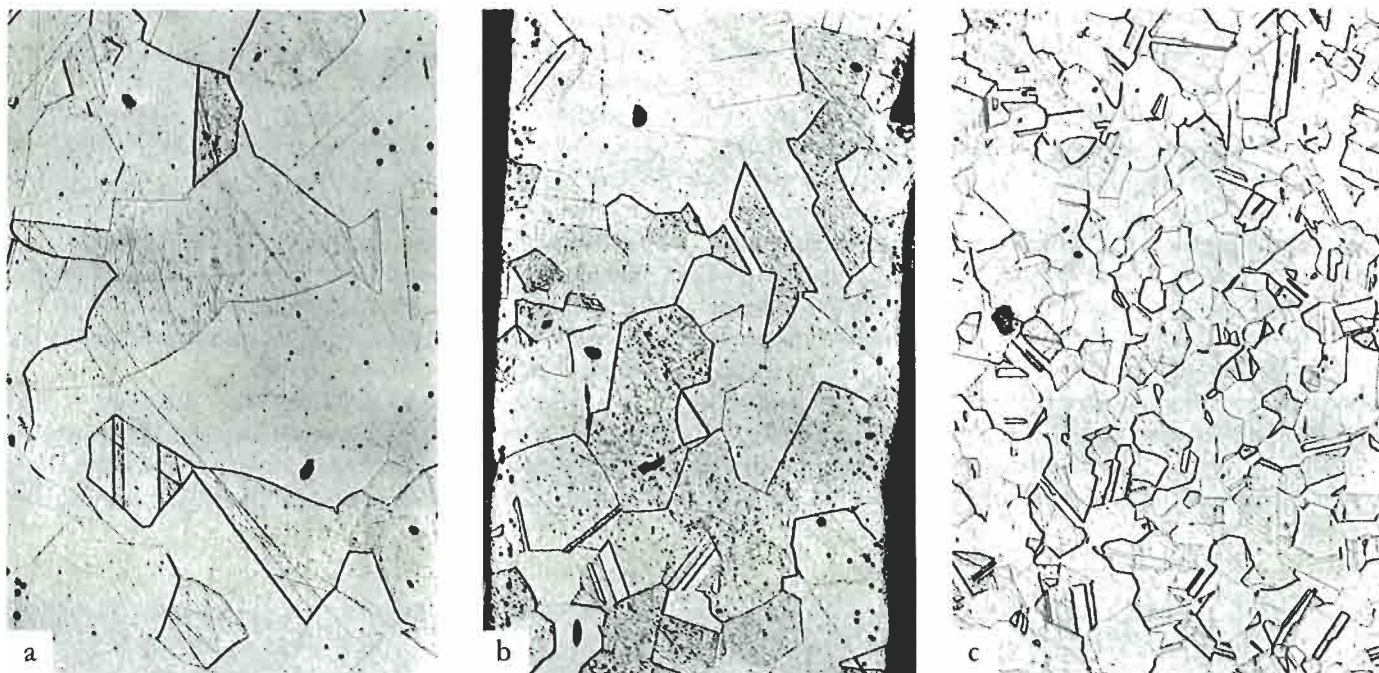
Fig. 3   Microstructure of a 14-carat Au-Ag-Cu-Zn alloy (a), and the same alloy with additions of 0.05% Ir (b), and 0.1% Co, 0.1% Ni, 0.05% Zr and 0.005% B (c) after annealing at 750 °C for 1 h

observed in this alloy was not much different from that shown in Figure 1 (c). Introduction of 0.1 per cent nickel has been found to produce more uniform grain structure without reducing the average grain size substantially. However, alloys with the complex cobalt-nickel-zirconium-boron addition showed higher hardness and lower plasticity than the unmodified alloy.

Addition of iridium produced drastic grain refining of the cast structure (Figure 1 (e)) and also substantially reduced the recrystallized grain size (Figure 2 (b), Table I) with both effects enhanced by a higher iridium content. It should be noted that the effect of iridium on grain size increases with increase of annealing temperature. However, prolonged (1 h) annealing at 750 °C is accompanied by a marked grain growth whereas only a slight increase in grain size occurs in the alloy with the above quaternary addition.

A fine-grained recrystallization structure in iridium-containing alloys is retained after threefold remelting. The grain refining effect of iridium on the cast structure was even enhanced by remelting (Figure 1 (e)). Iridium does not reduce alloy ductility. Tensile tests on 1 mm wire showed increased elongation and unchanged strength, whereas the Ericksen cup drawing test resulted in unchanged plasticity and enhanced strength.

In order to verify whether the grain refinement achieved by addition of 0.05 per cent iridium is adequate to prevent the formation of 'orange peel' the Ericksen test has been carried out on sheets of unmodified and iridium-containing alloy annealed for 15 min at 720 °C. As can be seen in Figure 4 a distinct 'orange peel'

pattern develops on the surface of the unmodified alloy whereas the iridium-containing alloy gives a satisfactorily smooth surface.

For the two alloys which demonstrated a significant grain refining effect, one containing 0.05 per cent iridium and the other with the complex quaternary cobalt-nickel-zirconium-boron addition, attempts have been made to determine the distribution of additives in the alloy by the use of transmission electron microscopy and electron probe microanalysis. However, neither of the techniques has proved to be effective, probably due to the very low concentration of the additives.

## Discussion

### Grain Refinement During Solidification

Two possible mechanisms for the effect of minor additions on grain refinement during solidification are considered here and can be summarized as follows:

(1) If minor additions of highly active elements react with the atmosphere, the crucible, other minor components of the alloy or with some uncontrolled impurities, minute solid particles of oxides, carbides etc. may be formed. On further cooling, these particles provide sites for so-called 'heterogeneous nucleation' of the alloy crystals, thereby diminishing the extent of supersaturation needed for solidification and increasing the number of growing crystals. This mechanism has been experimentally confirmed by X-ray observation of titanium carbide particles in an aluminium alloy containing 0.1 per cent titanium (16).

Fig. 4 Surface of a 14-carat Au-Ag-Cu-Zn alloy (left) and the same alloy with the addition of 0.05% Ir deformed by deep drawing (Ericksen cupping test, ball 3 mm dia.) after 15 min annealing at 720 °C. The smoothness of the surface of the Ir-containing alloy in comparison with the distinct 'orange peel' appearance of the unmodified alloy should be noted
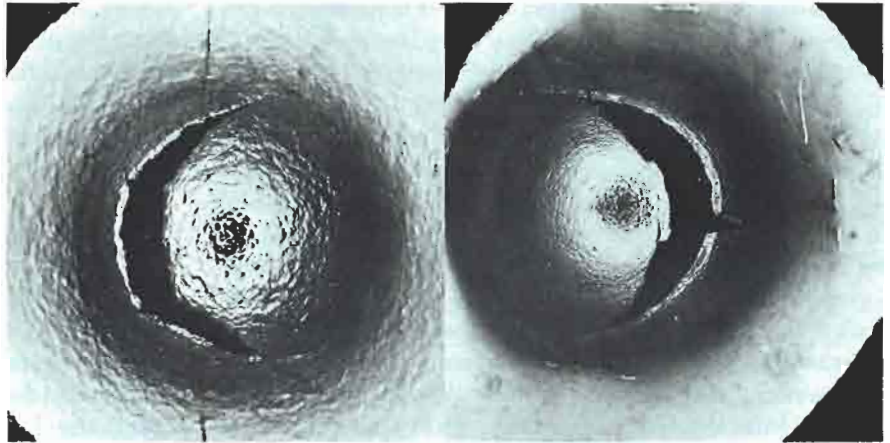
(2) If alloys of the additive element with the major component of the alloy are characterized by a phase diagram with a eutectic (or peritectic) point situated very close to the pure major component, even small amounts of the additive give an alloy of hypereutectic (or hyperperitectic) composition (Figure 5). In these alloys a certain temperature range $\Delta T_p$ exists between the liquidus and eutectic (peritectic) lines where primary crystals of the minor alloying component (or its compound with the major component) will precipitate. Due to a very low concentration of the minor addition very fine particles are formed and when the eutectic (peritectic) temperature is reached these particles will provide centres for heterogeneous nucleation and growth of the crystallites of the (essentially pure) major component.

An additional factor that accounts for a more effective grain refinement in alloys in comparison with pure metals (16) is the formation of a concentration gradient in the melt in front of the growing crystals. Due to a difference in composition between solid and liquid phases at a given crystallization temperature and a limited diffusion rate in the melt, the layer adjacent to the growing surface will become enriched with the component that preferably remains in the liquid phase. This compositional change decreases to a greater or lesser extent, in accordance with the liquidus slope of the equilibrium freezing temperature of the melt in the layer or, in other words, causes a retardation of crystal growth at a given cooling rate. Due to this, a greater number of potential centres of heterogeneous nucleation is activated on further cooling and better grain refinement is achieved. The wider the separation between solidus and liquidus curves and the steeper the liquidus slope, the greater the retardation of growth rate that occurs (17).

The well pronounced dendritic segregation observed in the 14-carat gold jewellery alloy studied (Figure 1 (a)) indicates that a significant compositional gradient develops during its solidification. This must enhance grain refinement where this effect is produced by minor additions according to one of the two mechanisms mentioned above.

Because of a lack of data, the mechanism by which small additions cause grain refining of the alloy studied will be discussed against the background of the available binary phase diagrams of the added metals with gold. It is assumed that this approach can be adopted because of the small amounts of additions used and due to the fact that at higher temperatures the quatenary alloy studied is a gold-based solid solution. Indeed, the observed behaviour of the 14-carat alloy with additions of iridium, boron, zirconium or cobalt during solidification is in agreement with that to be expected from the corresponding binary phase diagrams of the various added metals with gold (Figure 6). Compositions of all of the alloys studied containing boron, iridium and cobalt fall well into the hypoeutectic range so that no precipitation of boron, cobalt or $IrAu_3$ can occur during solidification. In contrast, alloys with 0.02 and 0.05 per cent iridium are hypereutectic and grain refinement induced by iridium precipitation at the first stage of solidification can be expected. The enhanced effect observed at the higher iridium content is probably due to a greater number of iridium precipitates formed in this alloy.

Fig. 5 General appearance of eutectic (left) and peritectic (right) binary phase diagrams with eutectic (peritectic) point very close to the component A. All compositions to the right of the dashed line are characterized by a temperature range $\Delta T_p$ between the liquidus curve and eutectic (peritectic) line where precipitation of primary crystals of $\beta$-phase (rich in component B) occurs. When eutectic (peritectic) temperature is reached these precipitates provide centres for heterogeneous nucleation of the crystals of the major component of the alloy, $\alpha$-phase
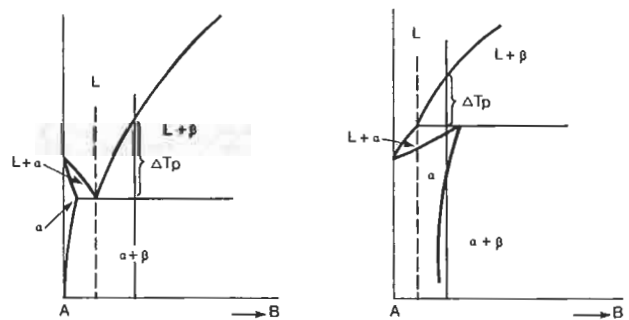
It can be also assumed that the positive effect of remelting is due to a more uniform iridium distribution achieved by remelting.

It should be noted that the grain refinement of pure gold at iridium concentrations as low as 0.002 per cent has been reported (2). To explain this result a mechanism of what can be called 'additive-assisted homogeneous nucleation in hypoeutectic (or hypoperitectic) alloys' has been proposed (2). This mechanism implies that elements dissolved in the melt and having a high melting point and low solid solubility will have a tendency to segregate from the melt on the surface of nuclei, lowering their surface energy and thus promoting nuclei formation at low supercooling. This mechanism, however, seems too hypothetical as it leaves unexplained why, at hypoeutectic compositions, the atoms of the additive should segregate to the nucleus surface and not remain in the melt, as expected from the equilibrium phase diagram. Although boron, zirconium and, probably, cobalt could be considered appropriate additives from the point of view of this mechanism, these elements did not produce any grain refining of the solidification structure in this investigation. It seems that the effect of 0.002 per cent iridium observed in (2) can be attributed either to the fact that the actual position of the eutectic point is closer to pure gold or, more probably, that a uniform distribution of

iridium in the melt was not achieved. The effect of remelting observed in this study seems to indicate that a uniform distribution of iridium is difficult to achieve even at much higher concentrations. It should be also mentioned that, according to J.P. Nielsen (18), about 0.015 per cent iridium is needed for grain refining of gold alloys.

### Retardation of Grain Growth During Annealing

It has been found that a wider range of additives have a grain refining effect on the annealed structure. As shown by short-time annealings (0.5 to 3 min) these additives do not influence the grain size observed just after the completion of recrystallization although some of them do increase the duration of this stage. The difference in grain size observed at longer annealing times is therefore due to the effect of additions on the rate of the grain growth process that follows recrystallization.

The additives studied can be divided into two groups according to their behaviour at the annealing temperatures:
(1) Iridium which is practically insoluble in the alloy and is probably present in the form of fine particles formed during crystallization
(2) The remaining additives which at the concentrations used are in the solid solution*.

According to theoretical predictions (19), both finely dispersed particles and solute atoms can affect the migration of grain boundaries and thus restrict grain growth, though by different mechanisms.

The driving force for grain growth in a recrystallized structure is the excess of energy associated with grain boundaries and it is inversely proportional to the radius of the boundary curvature. Fine particles cause a local increase in boundary length and thus create a drag of boundary motion. At a given volume fraction $f$ of the particles this effect is inversely proportional to the average particle radius $r$. Moreover, since the average boundary curvature, and hence the driving force, diminishes with the increase of average grain size, at some stage the particles can prevent further growth. The upper limit for the grain size $D_m$ in the presence of particles is:

$$D_m = 4/3 \ (r/f) \qquad (1)$$

For the alloy with 0.05 weight per cent iridium $f$ is $3 \times 10^{-4}$ and the effect of the additive depends on the degree of fineness of the iridium particles. If we assume their size to be $0.1\,\mu m$, the maximum grain size $D_m$ in this case is about 0.2 mm. It means that precipitates of this average size cannot prevent appreciable grain growth during prolonged annealing (as indeed occurred in the iridium-containing alloy after 1 h annealing at 750 °C) but the retardation of boundary migration produced could result in the grain refinement that was observed after annealing times of 15 min.

Fig. 6 Gold-rich part of the binary phase diagrams Au-Ir (2); Au-B (W.G. Moffat, 'The Handbook of Binary Phase Diagrams', vol. I., General Electric Company Publication, 1978); Au-Zr and Au-Co (M. Hansen and K. Anderko, 'Constitution of Binary Alloys', McGraw-Hill, N.Y., 1958, pp. 244 and 195)
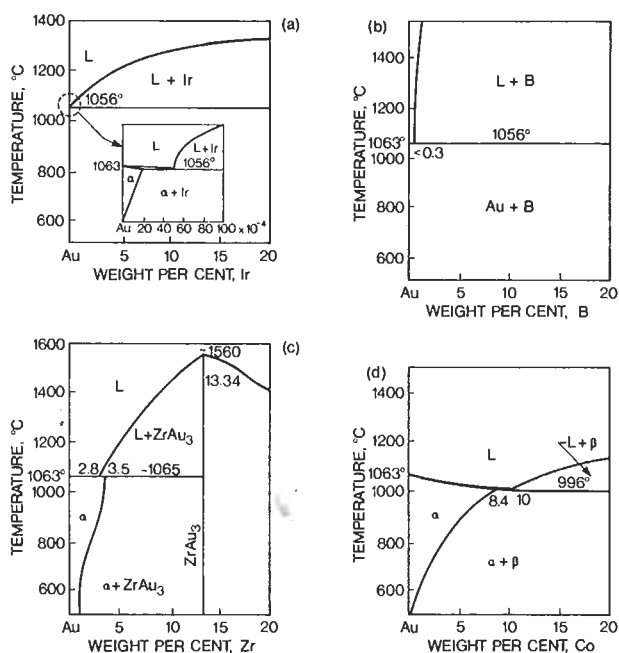


* The solubility of yttrium in gold is not known, but by comparing with the solubilities of rare earth metals in gold it is probably higher than 0.02 per cent at the annealing temperatures.

The retarding effect of very small amounts of *soluble* additives on grain boundary migration in pure metals is a well established fact (20). It is explained as an effect of segregation of solute atoms along grain boundaries accompanied by energy gain and described by the following equation:

$$C_B = C_o \exp(-E/RT) \qquad (2)$$

where $C_B$ and $C_o$ are boundary and bulk concentrations of the solute atoms respectively, $E$ is the interaction potential between the solute atoms and the boundary, $T$ is the annealing temperature. Because the boundary region is characterized by a less regular and less dense atomic structure, size misfit between the solute atoms and the matrix lattice is the most evident reason for the boundary segregation. It is likely, however, that other factors such as difference in valency or type and strength of interatomic bonds between host and foreign atoms can play some role, too, in the formation of the atmosphere of foreign atoms around grain boundaries. When such a boundary is caused to move, the interaction of foreign atoms with the boundary creates a drag and, unless the driving force for boundary movement is large enough, the boundary is compelled to carry the atmosphere of foreign atoms along with it. In this situation, the boundary velocity is controlled by the rate at which foreign atoms can diffuse behind the boundary (19, 20). Obviously, in spite of retardation of grain growth no upper limit can be imposed by boundary segregation of solute atoms on the grain size in annealings of long duration. The other difference between the effect of finely dispersed particles and that of boundary segregation is that the latter diminishes with the increase of annealing temperature as a result of both increased diffusion mobility of impurities and decreased tendency for grain boundary segregation, as follows from equation 2 above. It can be also expected that in the case of a quaternary gold-based solid solution the effect of soluble additives will be less pronounced than in pure gold.

However, the grain refining effect of soluble additives (or the lack of it) as observed in this investigation is not consistent with the theoretical predictions. Of four soluble additives introduced in various amounts (0.005 to 0.1 boron, 0.02 yttrium, 0.04 to 0.1 zirconium, 0.1 to 0.3 cobalt per cent only zirconium gave a moderate grain refinement whereas boron and yttrium, which represent two extremes of the size misfit in respect to the alloy lattice, had no effect at all. At the same time the lowest amount of boron used (0.005 per cent) can have a significant, though not easily reproducible, effect when added together with either 0.1 per cent of zirconium or cobalt, and the best grain refinement is achieved when it is combined with both 0.05 per cent zirconium and 0.1 per cent cobalt. It is evident that boundary segregation as described by equation 2 cannot account for the effect because the total bulk atomic concentration of the additives in this alloy is lower than in the many alloys in which the same additives were introduced separately without appreciable grain refining effect. Another observation inconsistent with the expected effect of the boundary segregation of solute atoms is that

of a low rate of grain growth which occurs at 750 °C (Figure 3).

The strong enhancement of grain refining observed in a 14-carat gold alloy when complex alloying with boron, zirconium and cobalt is used suggests that there must be an interaction between the additives resulting in a limited mobility of grain boundaries. As noted by Losch (21), chemical interaction between two solutes is most likely to occur at grain boundaries where it is promoted by a higher concentration of solute atoms resulting from their grain boundary segregation. Because boron forms borides with both zirconium and cobalt, it can be expected that it is precipitation of boride particles at the grain boundaries that reduces mobility of the boundaries and prevents extensive grain growth in the gold alloy containing additions of these metals.

## Conclusion

The grain refining effect of various elements — iridium, zirconium, cobalt, boron and yttrium — added in small amounts, singly or in various combinations, to a 14-carat gold-silver-copper-zinc alloy has been investigated in both solidified and recrystallized structures. It has been found that only additions of iridium give a strong and reproducible grain refinement of the as-cast structure. Ternary addition of cobalt, zirconium, and boron as well as additions of iridium restrain significantly grain growth during annealing in the temperature range 600 to 750°C, and effectively prevent formation of 'orange peel' during subsequent cold working. The effect of iridium on both as-cast and annealed grain size is ascribed to finely dispersed iridium particles which precipitate from the melt at the earliest stage of the alloy solidification. The retardation of grain growth during annealing produced by the ternary addition is believed to be due to the formation of boride precipitates stimulated by grain boundary segregation of the additives.

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