Grain Size of Gold and Gold Alloys

A REVIEW AND SOME RECENT DEVELOPMENTS

Dieter Ott and Christoph J. Raub

Forschungsinstitut für Edelmetalle und Metallchemie, Schwäbisch Gmünd, Federal Republic of Germany

Although the use of grain refining agents in dental gold casting alloys is well documented, little has been written concerning the use of such agents in casting and other gold alloys used in jewellery fabrication. This review of the control of grain size in gold alloys includes reference to recent findings regarding the use of cobalt in carat gold alloys.

The structures of gold and its alloys, like those of other metals, are determined in many respects by the thermal, mechanical and other treatments to which they have been subjected. The structure of an ingot in the as-cast condition, for example, is typical and different from that of the metal after cold working, and this again differs from that which is formed on cold working and annealing (Figure 1). Grain size is a particularly important aspect since it can significantly affect several important properties of metals and alloys. An understanding of the factors which determine this variable is therefore of considerable importance.

Solidification Structures

When a metal or alloy solidifies from the molten state, as in casting for example, its structure is determined by the processes of nucleation and dendritic growth (1). The growing dendrites are variously oriented in the liquid metal and where they come into contact with one another grain boundaries are formed. The solid, therefore, is polycrystalline and the boundaries which separate the grains that are formed around each of the nuclei are interconnected in a honeycomb arrangement. The sizes of the grains and their shapes and orientations are determined by such factors as the rates of nucleation and dendritic growth, and by the tendency of crystals to form initially on the cold walls of the mould and to grow inwards towards the centre of the casting. In the case of alloys which solidify over a range of temperatures, differences in composition may occur both within individual grains and/or from grain to grain. The

former are due to differences in composition of liquid and solid which are in equilibrium at any one temperature, thus causing the nuclei of the dendrites to be richer in the high-melting component than the outer regions that are formed subsequently. The latter differences in composition arise when solidification occurs with the formation of two distinct solid phases in equilibrium with one another. Finally, with both metals and alloys there is a tendency for impurities to accumulate in the last of the liquid phase which solidifies at grain boundaries and in the interdendritic spaces. This can have an adverse influence on the properties of alloys, particularly in cases where they are coarse-grained.

In precious metals technology a structure is generally regarded as coarse if the average grain diameter is greater than about 0.35 mm and as fine if it is less than 0.1 mm (2).

In tune with experience gained from alloys of other metals, fine-grained as-cast gold alloys show many advantages over coarse-grained ones (3). Their surfaces are more easily polished, they have improved tensile properties and they maintain their integrity better when cast into sharp-edged or cornered shapes. Moreover, fine-grained castings are far less likely to crack during rolling and can therefore be more heavily deformed before annealing becomes necessary. Further, they have the important advantage of being more consistent in properties from melt to melt (4). Thus, means for controlling the grain size of gold alloy castings are of considerable practical importance. It is surprising therefore, that although grain refinement has been studied and applied extensively in dental gold casting alloys (2) and in electronics (5), it has received much less attention in the production of cast gold jewellery, in which the problems caused by large grain size have long been recognized (6).

Recrystallization Structures

In processes such as swaging, hammering, rolling and drawing which are commonly used in the mechanical processing of cast ingots, metals and their alloys are deformed. The cast structure is broken down and the material becomes progressively harder and more difficult to work, as lattice defects increase in number. The metal or the alloy must therefore be

Fig. 1 Microstructure of a 14 carat (58.5 gold/30 silver/11.5 copper weight per cent) alloy, in the as-cast condition (left), after 70 per cent deformation (middle) and after deformation followed by annealing for 1 h at 700°C (right) x 100

annealed at appropriate stages in the deformation processes, in order to soften it and render it more amenable to further deformation. In the annealing process, recrystallization occurs and a new structure develops, the characteristics of which depend both on the extent of prior deformation and upon the temperature and duration of the anneal (7).

If the deformation produced by prior cold working has been small (less than 20 per cent), then the energy stored in the form of lattice defects may be insufficient to promote complete recrystallization of the metal during annealing, though some existing grains may grow during the process. If cold working has been adequate (typically to 70 per cent deformation), then recrystallization to a different structure occurs during annealing (Figure 1). The process of recrystallization does not cease at this point, however, and if annealing is carried out for too long or at too elevated a temperature, grain growth occurs and a coarsening of the fine-grained recrystallization structure quickly ensues.

Specific hardness ranges, which are often required for semi-finished products such as wire or plate, can thus be achieved in two ways: either by annealing the deformed material for a predetermined time at appropriate temperature, or by deforming the fully recrystallized, soft material until the required hardness is achieved. The first procedure has the disadvantage that in most alloys the transition from the hard to the soft state occurs rapidly at the annealing temperatures which are common in production. In general, the second procedure is therefore preferred. Whichever method is used, however, the final product must be fine-grained in order to achieve optimum performance characteristics.

The classic manifestation of coarse grain size in gold alloys is the 'orange peel' effect. This is characterized by the development during deformation of the material of a surface appearance similar to that

of an orange skin. It results from a shifting of individual coarse grains relative to one another, in extreme cases to such an extent that the grain boundaries become apparent to the naked eye. Orange peel effects call for extra work in polishing or repolishing of final products and this may result in excessive wear of tools and in loss of alloy. Thus, if a gold alloy is clad on a base metal substrate and has a coarse-grained structure when the cladding process is complete, the orange peel effect which develops during the subsequent deformation of the composite product (for example, in the production of a watch case) may be so severe as to require polishing to the point where the gold alloy coating itself is worn through (8).

Grain size can also be critical in the drawing of the very fine wires, 7.5 to 50 μm in diameter, which are used in electronic circuitry. A fine-grained material is less liable to break during drawing than one of coarse structure, and it retains its mechanical strength to higher temperatures. Special measures have been described which favour the formation of fine grain structures in pure gold as used in the production of very thin wire (5).

Grain Refinement during Solidification

Grain refinement of alloys during solidification from the molten state can be achieved in two ways; either by promoting the formation of large numbers of nuclei for grain growth, or alternatively, by incorporating in the melt additives which decrease the rates of grain boundary migration and the rates of growth of grains once nuclei have been formed.

Heterogeneous Nucleation

In the first method, nuclei for grain growth are introduced into the melt. In the inoculation of the melt, however, it is difficult to ensure uniform distribution of the nuclei and to avoid their agglomeration or their rising or sinking in the liquid alloy. This applies even

in cases where the inoculum is a metal that is soluble and oxidizes readily in the melt to form finely dispersed oxide particles. Furthermore, inoculated alloys tend to give rise to problems during operations such as polishing or milling and on solidification after remelting (even in welding), owing to the agglomeration of the additives at grain boundaries.

Special Casting Methods

It is known in the trade that 'cold pouring', mould vibration and agitation, and gas-melting, produce fine-grained castings. By cold pouring, nucleation is enhanced and grain growth retarded. By vibration and agitation of the melt, nuclei are more evenly distributed or grains that have formed are broken up. The practical observation that grains in gas-melted alloys tend to be smaller than, for example, in induction-melted ones is probably due to the absorption of impurities such as carbon-containing gases.

Homogeneous Nucleation

In homogeneous nucleation, nuclei are produced within a supercooled liquid by the segregation during solidification of additives that were previously dissolved in the melt. Theoretical free energy considerations indicate that elements having high melting points and low solid solubilities should be especially suitable for this purpose (2). This is the case for ruthenium, iridium, rhenium, molybdenum, tungsten and cobalt, for example, which have been used as grain refining agents in dental gold casting alloys for a number of years (2, 4). For such grain refiners there is usually a critical, but low concentration above which no further refining effect occurs. This is demonstrated in Figure 2 which shows the grain size of gold against concentration of dissolved ruthenium and iridium.

It is often difficult to ensure that the distribution of refractory metals in the melt is completely uniform and that their concentrations are kept under accurate control. Problems also arise in the remelting of scrap containing too high a concentration of the additives, or with incorrect temperature control during casting and solidification leading to the segregation of coarse particles of the additive.

Although gold alloys in which the formation of a fine-grained structure has been promoted by the introduction of nuclei into the melt find wide application in current dental casting technology, they are not used in gold jewellery manufacture. This is largely due to the problems which are associated with the presence of segregated materials or inclusions, especially the difficulty in achieving the high quality surface finish which is demanded of jewellery. Thus, even the small oxide inclusions which can act as nuclei for grain growth in dental castings cannot be

Fig. 2 The effect of ruthenium and iridium on the grain size of gold in the as-cast condition, after (2). Grain refining occurs as a result of homogeneous nucleation

tolerated in most jewellery applications. The same applies if silicon is used as a grain refining agent in combination with silicide-forming metals, or if poorly soluble metals such as molybdenum, tungsten, iridium or rhenium are added and their concentrations are not carefully adjusted so as to avoid excessive segregation. Such additions also lead to complications if scrap is re-melted for direct use. Homogeneous nucleation can therefore be used as a method for grain refining gold jewellery alloys only if it can be carefully controlled.

Grain Refinement in the Solid State

In gold, as in aluminium alloys, it has been found that certain elements in solid solution can strongly hinder grain growth during recrystallization, thereby ensuring a fine-grained structure (3, 5). This may be ascribed to an interaction between the dissolved additives and the grain boundaries of the host matrix, as a consequence of which the added elements accumulate at grain boundaries (3, 9). Thus, the migration velocity of the grain boundaries is determined in considerable measure by the rate of migration of the foreign atoms. At very low concentrations and at high temperatures the interaction is very small, hence the movement of the grain boundaries is rapid and recrystallization and grain growth are unrestrained. When the concentration of the additives exceeds a certain critical value, however, the interaction becomes significant, recrystallization rates are diminished and the recrystallization temperature of the alloy is raised. It is characteristic of the effect that the influence of the foreign atoms on the process of

recrystallization increases with the difference between the atomic radii of the foreign and host atoms.

To some extent, this interpretation of the phenomenon discussed here does not differ greatly from that derived from free energy considerations (2). The basic facts have, however, been confirmed in a systematic investigation into the effects of more than 20 elements on the grain size and recrystallization behaviour of gold and various carat gold alloys (10). The results have already been applied in the production of novel alloys in which grain growth during jewellery fabrication processes can be very satisfac-

torily controlled (11). It was found that certain elements act as grain refiners of gold and gold alloys in specific concentration ranges which depend on the composition of the host alloy. At higher concentrations, however, the same elements may cause excessive grain growth, as exemplified by the effects of iron or chromium additions to carat gold alloys (12).

There are certain limitations which must be borne in mind in the use of grain growth-retarding additives in the industrial production of wrought gold jewellery, namely:

- (1) The added elements should be amenable to melting in equipment that is normally available in factories producing gold jewellery. This eliminates the use of certain refractory elements which form carbides or oxides with crucible materials, such as the elements of Groups III, IV and V of the periodic system. This problem can be overcome partially by introducing the elements in the form of highly dilute master alloys. For example, titanium or zirconium can be added to jewellery alloys in the form of their dilute alloys with gold, silver or copper
- (2) They must dissolve easily and completely in the melt. This is rather difficult to achieve with additions of refractory metals such as rhenium, molybdenum, tungsten, ruthenium and iridium, even if nickel- or palladium-based master alloys are used, since they are insoluble in gold, copper and silver — the main constituents of carat gold alloys. If they are not dissolved properly very hard aggregates may form, as discussed above
- (3) They should not oxidize preferentially in relation to the main alloy constituents. If they do, then there exists the danger of the reduction in their concentrations during melting and annealing, as well as that of the occlusion of oxide particles
- (4) They should not complicate the processing and refining of scrap
- (5) They should not be detrimental to the properties of the host alloy in respect of such operations as welding, soldering and polishing

Fig. 4 The effect of the addition of cobalt on the microstructure of a 14 carat (58.5 gold/30 silver/11.5 copper weight per cent) alloy deformed by 70 per cent and annealed for 1 h at 700°C. The cobalt-free alloy (left) is coarse-grained, whereas the alloy containing 0.2 weight per cent cobalt (right) has retained its fine structure x 100

Fig. 5 Deep drawing, in the Erichsen cupping test, of the 58.5 gold/30 silver/11.5 copper weight per cent alloy

Top: Microstructure of the undeformed alloy sheets, free of cobalt (left) and with the addition of 0.2 weight per cent cobalt (right) x 100

Bottom: Surfaces of the corresponding deformed alloys x 2

Note that the fine structure of the cobalt-containing alloy prevents the occurrence of the 'orange peel' effect

- (6) Their concentrations in the alloys should be easily determinable without the use of expensive equipment.

In the course of investigations by the authors and their associates (10, 11, 12), the findings of Masing, Lücke and Nolting (3), and of Lücke and Detert (9) were confirmed in regard to the grain refining effects which numerous elements have on fine gold and various 14 and 18 carat alloys. In some cases, however, the refining action of an element was found to be inhibited by the presence of minor quantities of other elements. This might explain the inconsistent observations that are sometimes made in practice, in which ingots prepared from the same starting materials are fine-grained in one casting and coarse in another. Although such behaviour may be caused by slightly differing thermal conditions during casting, it may equally well result from differences in the trace impurities taken up during melting.

The Choice of Cobalt

At certain concentrations, cobalt, barium and zirconium are very effective grain refiners in the recrystallization of gold and gold alloys (10, 11, 12). While it is difficult to control the concentrations of barium and zirconium, because of their reactions with oxygen or with crucible materials, especially during remelting of scrap, this is not the case with cobalt. This metal dissolves relatively easily in liquid gold alloys, especially if it is introduced in the form of a

gold/10 cobalt weight per cent master alloy. With a little care this master alloy can even be prepared in normal clay-graphite crucibles under inert gas or charcoal blankets.

The cobalt concentration can be easily held to within the critical level by testing the alloy (which is normally not ferromagnetic) for ferromagnetism. When the critical concentration corresponding to the solvus line in Figure 3 is exceeded, cobalt-rich ferromagnetic aggregates form in the alloy and a small permanent magnet hanging on a thread adjacent to the cast ingot is deflected. (This method is not applicable to ferromagnetic gold-nickel alloys.) It is found from experience during production, that a certain very small deflection of a known magnet is an indication that cobalt is present in the correct concentration and that it is uniformly distributed. In practice, cast bars should be virtually non-magnetic. This means that the concentration of the cobalt in solid solution must be close to that given by the solvus line in Figure 3 — for example 0.2 atomic per cent at 400°C, if annealing is carried out at this temperature. The critical concentration of cobalt is, however, to some extent dependent upon the rate of cooling during casting or annealing.

Carat gold alloys containing such concentrations of cobalt are very fine-grained, even in the as-cast condition. More important is the fact that the fine-grained structure is retained after cold working and annealing (Figure 4). Figures 5 to 7 clearly illustrate the fine

Fig. 6 Unpolished, deep drawn, rectangular watch cases manufactured from the 58.5 gold/30 silver/11.5 copper weight per cent 14 carat alloy

Top: Surface finish of the cobalt-free alloy (left) and of one containing 0.2 weight per cent cobalt (right) x 1.5
Bottom: The surfaces of corner portions of the same watch cases, observed by SEM x 50

The presence of cobalt again leads to a surface free from 'orange peel' and thus requiring far less polishing

grain structure of cobalt-containing gold alloys that have been subjected to cupping tests — intended to demonstrate their suitability for the manufacture of watch cases — and to sizing tests on wedding rings. It will be appreciated from the illustrations how much easier it is to polish a fine-grained material than a coarse-grained one. Moreover, when a ring made of the fine-grained alloy is expanded by several numbers, the texture of its surface is not affected and it does not need to be repolished.

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Fig. 7 Surface finishes of 18 carat (75 gold/15 silver/10 copper weight per cent) wedding rings expanded by 10 numbers after completion of manufacture. The pronounced roughening that occurs with the cobalt-free alloy (left) is prevented by the addition of 0.2 weight per cent cobalt to the formulation (right) x 50