

Platinum Investment Casting Alloys

NEW MATERIALS WITH IMPROVED PROPERTIES AND CASTING CHARACTERISTICS

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The high melting point of platinum makes stringent demands on the other materials involved when it is investment cast. However, by careful selection of refractories, it has been possible to successfully cast small batches of platinum items for many years. In view of the renewed interest in platinum jewellery it has now become desirable to increase the efficiency of the process, and a number of new platinum alloys have been developed for this purpose. In some the alloying elements are those traditionally associated with platinum but in others more unusual additions are used to produce alloys with a significantly lower casting temperature.

Investment casting is a development of the very old lost wax method used by the ancient Greeks and Chinese over two thousand years ago. The name, lost wax casting, owes its origin to the fact that an expendable wax pattern was formed of the object to be cast. When this had been surrounded by a heat resistant mould material the pattern was melted out and the wax was "lost".

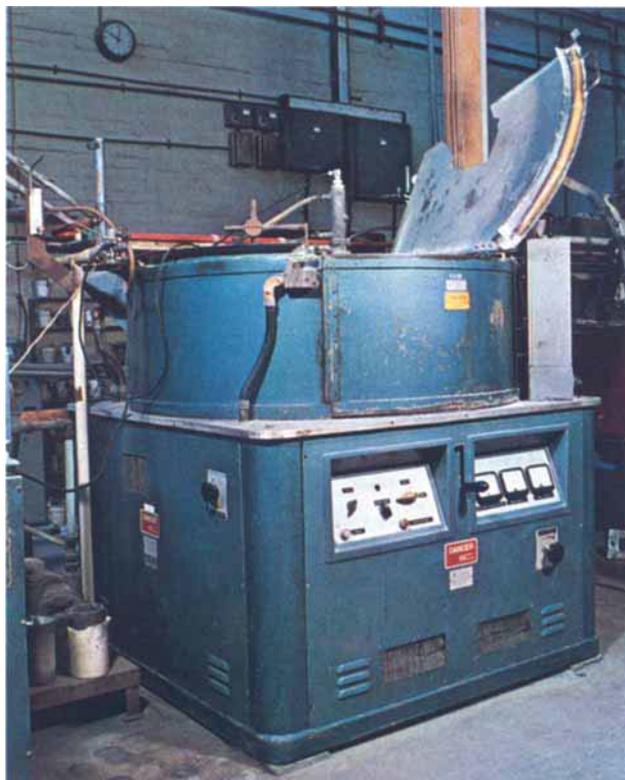
Today the process is highly sophisticated, enabling thousands of replica castings of one item to be manufactured cheaply, by-passing the need for soldering, sawing, filing or the numerous other operations generally involved when jewellery is fabricated from wrought material. Using the original master pattern a rubber mould is formed and in this the required number of replica wax patterns are produced. If the castings are to be made from a material having a melting point below about 1300°C the replicas are next assembled onto a wax tree. This becomes the pattern for the refractory investment casting mould which is supported by a steel flask. The material to be cast can be melted by induction

or air/fuel gas heating, and to ensure satisfactory filling the molten metal is forced into the previously fired flask, generally by centrifugal means. This technique enables a substantial number of castings to be produced from a single melt and, providing the many stages of the process have been adequately controlled, the castings will possess all the fine detail present on the original master pattern. Equipment suitable for the investment casting of both gold and platinum alloys is shown in Figure 1. The most important of the platinum alloys at present used for investment casting was developed to conform to the United Kingdom Hallmarking Act of 1973; all have melting ranges between 1725 and 1780°C and at these temperatures a modified process is required.

Platinum Casting Process

The effect of the very much higher temperatures involved introduces many difficulties into the casting of platinum. The investments used for casting lower melting point materials are generally based on crystobalite/gypsum

Fig. 1 While some of the casting trials were made with simple equipment most were carried out on the sophisticated machine shown here. The charge is melted by induction heating and then thrown into the mould by a motor driven centrifuge. A radiation pyrometer mounted vertically above the melt gives an accurate measurement of temperature, and a gas probe can be used to introduce a protective atmosphere when this is required



mixes; for platinum a more refractory material is required and compositions based on silica with additions of phosphate based bonding agents are at present used. These more complex high temperature materials require considerably more preparation, including quite prolonged setting and drying periods. Even so the strength of these investments at elevated temperatures is low and it is therefore not practicable to cast a large number of items on one tree, as is possible when casting gold and silver alloys. In general only a few items are cast at one time, on a button rather than a tree, and each has to be well separated from the others to avoid further weakening the investment mould. Typical arrangements of platinum alloy castings on buttons are shown in Figure 2.

This configuration has a deleterious effect on the platinum casting process as it results in a small amount of metal being thrown into

a relatively large and very much cooler mass of investment. The resultant quenching effect on the molten platinum alloy, and the high thermal gradients involved, necessitate a superheat of between 250 and 400°C, that is temperatures in excess of 2000°C in the molten metal prior to casting, to ensure filling of each pattern in the mould. Clearly the thermal losses would be less if the temperature differential between the hot flask containing the mould and the molten metal could be reduced, but the inherent properties of the platinum investment restricts the temperature to which the mould can be preheated to about 900°C. However, a more refractory investment material that may be capable of withstanding higher preheat temperatures, and be more durable at the metal/investment interface, is currently under development in the United States of America. If successful this material will alleviate to some extent a number

of the problems faced by the platinum investment-caster.

Other aspects of the process also have to be changed from those used for gold and silver; for instance oxygen rather than air is required for torch melting operations and a highly refractory crucible is necessary, the clay/graphite type generally used for investment casting being unable to withstand the temperatures involved.

Alloy Development

Currently the major platinum alloy used in Britain in both wrought and cast form for jewellery manufacture is 4.5 per cent copper-platinum. A slightly harder alloy, 4.5 per cent ruthenium-platinum, is used to a lesser extent, mainly in wrought form.

The copper-platinum alloy has basically acceptable mechanical properties for a casting material, being resistant to the deformation which could result from the stresses present in the mould as the metal solidifies and yet being amenable to subsequent sizing and setting operations. However, our experience in casting this alloy has suggested that it is not completely satisfactory. When in the molten state in air a copper oxide skin forms, and this reduces the fluidity of the alloy

making filling of fine section items difficult and producing a dull grey coloration on the resultant castings. In addition, predominantly with thicker section items, metal-mould reaction occurs causing surface roughness on such castings.

Clearly some further development was required to optimise the process and exploit any increase in the demand for platinum jewellery. This work took two forms covering both the development of an improved high temperature casting alloy and an evaluation of potential lower melting range materials designed to alleviate some of the problems and restrictions associated with the standard process.

1. High Temperature Alloys

For this part of the work a range of casting patterns was selected that would enable an assessment to be made of the most important properties. For example signet rings weighing 40 grams were cast to assess metal-mould reaction, as this was considered to be most likely to occur with a combination of high temperature and large mass of molten metal. In contrast settings for gem stones, weighing as little as 0.5 gram, were cast to determine alloy fluidity. In addition, conventional

Table I
Mechanical Properties of Platinum Casting Alloys

Alloy composition weight per cent	Hardness H _v	Ultimate tensile strength MN/m ²	0.1% Proof stress MN/m ²	Elongation per cent
4.5 Cu-Pt	108	318	190	20
4.5 Ru-Pt	114	383	248	14
1 Ir-3.5 Pd-Pt	60	167	100	30
4.5 Ir-Pt	73	205	139	22
10 Ir-Pt	113	329	239	10
4.5 Pd-Pt	68	167	93	22
15 Pd-Pt	64	187	103	22
1 Rh-3.5 Au-Pt	90	249	153	30
4.5 Co-Pt	134	400	182	20
1 Ni-3.5 Pd-Pt	82	218	139	20
2 Ni-2.5 Pd-Pt	104	465	309	18

Table II
Relative Quality of Castings Produced

Alloy composition weight per cent	Large signet rings (40 g)	Engagement rings (10 g)	Fine patterns and settings (approx. 0.5 g)
4.5 Cu-Pt	P	S	P
4.5 Ru-Pt	VP	P	P
1 Ir-3.5 Pd-Pt	VG	VG	VG
4.5 Ir-Pt	G	G	VG
10 Ir-Pt	G	VG	S
4.5 Pd-Pt	P	VG	VG
15 Pd-Pt	VP	S	S
1 Rh-3.5 Au-Pt	P	P	P
4.5 Co-Pt	VG	VG	VG
1 Ni-3.5 Pd-Pt	VG	VG	VG
2 Ni-2.5 Pd-Pt	S	S	S

VG—Very Good; G—Good; S—Satisfactory; P—Poor; VP—Very Poor

tensile test pieces were cast and the mechanical properties of each alloy determined. Other properties evaluated were ability to reproduce detail, colour and hardness.

The alloy compositions chosen for evaluation included several of United Kingdom Hallmarking quality in addition to other casting alloys at present used in the United States of America (4.5 per cent ruthenium-platinum and 10.0 iridium-platinum) and in Japan (15.0 per cent palladium-platinum). All are listed in Table I, together with their mechanical properties.

As an oxidation resistant casting alloy would have clear advantages the first investigations were carried out on alloys of platinum with additions of only other platinum group metals. Some of these alloys demonstrated casting characteristics superior to those of 4.5 per cent copper-platinum, as shown in Table II. In particular, all castings produced in 1 per cent iridium-3.5 per cent palladium-platinum were free from the effects of metal-mould reaction and had smooth, bright and sound surfaces. The absence of an interfering oxide film was demonstrated by its ability to fill very fine patterns and to reproduce detail.

The quality of castings produced in the two binary iridium-platinum alloys was only marginally inferior. Some very slight surface erosion was observed in the large patterns through metal-mould reaction and in the case of the 10 per cent iridium-platinum alloy, a proportion of the fine sectioned patterns were difficult to fill, both of these effects probably being a function of the higher casting temperature required. Castings in 4.5 per cent palladium-platinum were also superior to those in 4.5 per cent copper-platinum.

All these alloys have limited use, however, in casting application, their poor mechanical properties as shown in Table I resulting in the items being easily distorted during the casting process and subsequent handling.

The surface appearance of the 15 per cent palladium-platinum buttons suggested that considerable gas was absorbed during melting and subsequently evolved during solidification. Large and medium sectioned patterns were consequently seriously affected by porosity and extensive surface roughness demonstrated metal-mould incompatibility.

Although the mechanical properties of 4.5 per cent ruthenium-platinum were of the



Fig. 2 Two typical platinum buttons show the limited number of well-spaced items that can be satisfactorily cast at the elevated temperatures involved

order required for general purpose applications, most of the castings produced suffered from an intolerable degree of surface roughness and fine sectioned patterns were difficult to fill. Surface erosion was most extensive in the signet ring, an example of which is shown in Figure 3. Microprobe examination of the affected region revealed no chemical reaction and therefore the breakdown must have been purely mechanical.

As an extension of the all noble metal approach an alloy composed of 1 per cent rhodium-3.5 per cent gold-platinum was assessed. Both rhodium and gold have a hardening effect on platinum when present in binary alloys but the poor surface condition of the castings made this alloy unattractive.

Having explored thoroughly alloys containing only noble metals, base metal additions were next considered. Nickel, when added to platinum, imparts a significant increase in hardness and so in an attempt to retain the advantages gained in casting quality by the inclusion of palladium, two alloys, one containing 1 per cent nickel-3.5 per cent palladium-platinum and the other 2 per cent nickel-2.5 per cent palladium-platinum were evaluated. The product quality in 1 per cent nickel-3.5 per cent palladium-platinum was comparable to that of 1 per cent iridium-3.5 per cent palladium-platinum and there was

no evidence of surface oxidation. The increase of strength and hardness was not, however, sufficient for the application. Conversely the mechanical properties of 2 per cent nickel-2.5 per cent palladium-platinum are ideal but the casting quality was no better than 4.5 per cent copper-platinum, and the colour of the castings was characterised by a dull grey appearance resulting from base metal oxidation. In the large sectioned pattern the surface topography was very irregular due to the metal-mould reaction while porosity was rather more prevalent than in other alloys.

These results suggested that a binary alloy where the addition element hardens platinum to a lesser degree than nickel and which is oxidation resistant, might fulfil our requirements. It seemed that cobalt could be such an additive, and subsequent trials revealed that castings in 4.5 per cent cobalt-platinum were comparable in quality to both 1 per cent iridium-3.5 per cent palladium-platinum and 1 per cent nickel-3.5 per cent palladium-platinum, while the mechanical properties were in the preferred range for an alloy to be used in general purpose applications.

2. Lower Melting Point Alloys

As previously stated the platinum alloys at present used for investment casting have melting ranges between 1725 and 1780°C,

and therefore require a casting temperature of at least 2050°C to ensure satisfactory filling of fine sections. Even when the highest quality investment materials are used their properties are only just adequate for casting a few patterns at a time. To make the casting of platinum a less critical and more economic process, an improved investment material, with better high temperature properties, is therefore required. Alternatively or in addition to this, the development of a platinum alloy requiring a lower casting temperature would extend crucible life and permit more castings per button.

The possibility of developing platinum casting alloys with a significantly reduced melting range has now been explored, the two major objectives being to satisfy the 1973 Hallmarking Act and to obtain the properties required by the manufacturing jeweller.

Initially the effect of additions such as silicon and boron were evaluated. Molten platinum readily reacts with these elements to form low melting point eutectics, and therefore stringent precautions are generally taken to prevent them coming into contact. The eutectic silicon-platinum alloy, at 4.2 per

cent silicon, melts at 830°C and could consequently be air/fuel gas torch melted and cast in standard low temperature investments without undue difficulty; similarly the 2.1 per cent boron-platinum alloy with a melting point of 789°C could also be easily cast. Predictably the hardness of these alloys, 440 H_v and 327 H_v, respectively, coupled with their extreme brittleness rendered them unsuitable for subsequent fabrication. Figure 4 shows the dark coloured, hard, interdendritic constituents that occurred in the microstructure of an as-cast eutectic alloy.

Attempts to modify the structure by ternary and quarternary additions while retaining the reduced melting range, did not reduce the overall hardness of these materials below about 300 H_v and the castings were therefore unacceptable.

The relevant phase diagrams were examined for an element that, on alloying, could substantially reduce the melting point of platinum without exceeding the 5 per cent addition limit. Gallium appeared to do this, although not to the same extent as silicon and boron, and it offered the possibility of forming alloys having mechanical properties within



Fig. 3 The surface erosion, seen on the heavier sectioned ring cast in 4.5 ruthenium-platinum, results from breakdown of the investment. On the lighter sectioned ring this reaction is minimal

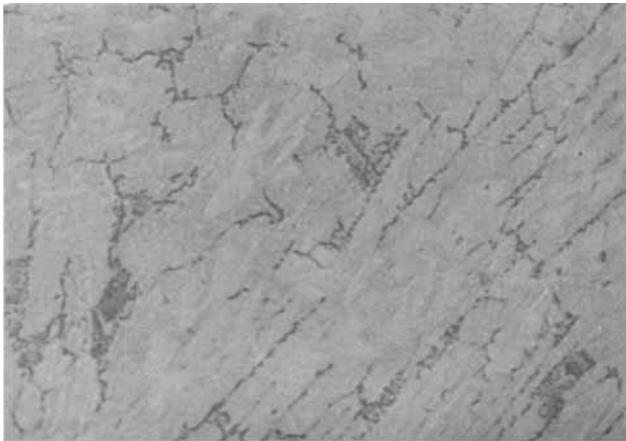


Fig. 4 The microstructure of a 4.2 per cent silicon-platinum ring cast at about 1000°C shows the very hard eutectic compound which made this experimental alloy unsuitable for most jewellery investment casting applications

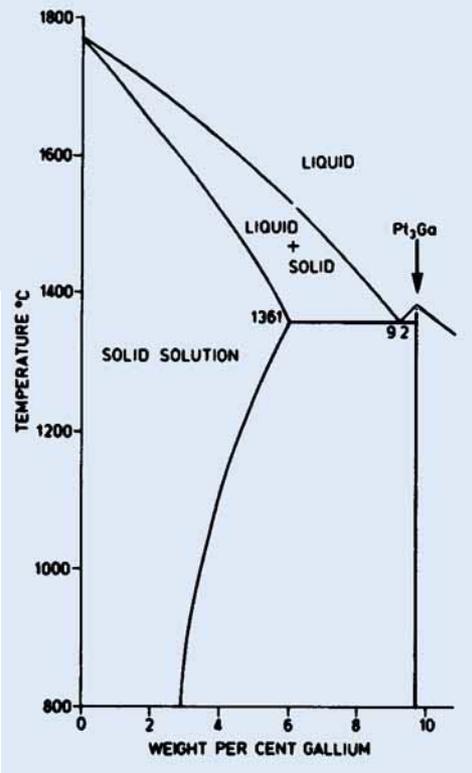
the range that might be acceptable to manufacturing jewellers. The relevant part of the phase diagram is shown in Figure 5. A series of exploratory binary alloys covering the range 2 to 5 per cent gallium-platinum were

therefore evaluated, the melting range and as-cast hardness values being given in Table III. Increasing the gallium content resulted in lower melting temperatures, but also increased the hardness values to such an

Alloy composition weight per cent	As-cast hardness H_v	Solidus temperature °C	Liquidus temperature °C
2 Ga-Pt	130-142	1650	1730
3 Ga-Pt	153-160	1550	1640
3.5 Ga-Pt	292-304	1525	1620
5 Ga-Pt	354-360	1440	1580

Alloy composition weight per cent	As-cast hardness H_v	Solidus temperature °C	Liquidus temperature °C
1 Au-4 Ga-Pt	360	1500	> 1600
2 Au-3 Ga-Pt	183	1560	> 1600
2.5 Au-2.5 Ga-Pt	171	1560	1620
3 Au-2 Ga-Pt	134	1580	> 1600
2.5 Pd-2.5 Ga-Pt	154	1580	> 1600
1 Ag-4 Ga-Pt	290	1490	> 1600
2.5 Ag-2.5 Ga-Pt	145	1525	1590
3 Ag-2 Ga-Pt	130	1560	> 1600

Fig. 5 The platinum rich end of the platinum-gallium phase diagram, as determined by P. Guex and P. Feschotte (J. Less-Common Metals, 1976, 46, (1), 109) shows the steep boundaries defining the liquid and solid phases. These, together with the narrow freezing range—where both liquid and solid exist—and the reasonable amount of solid solution possible, provide a sound basis for a lower temperature investment casting alloy conforming to the 1973 Hallmarking Act

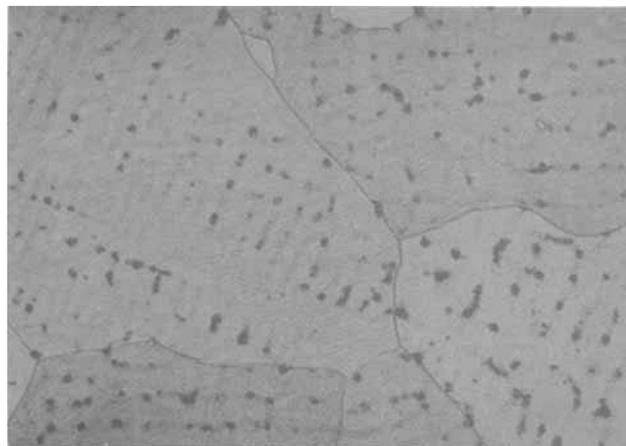


extent that alloys containing 3.5 per cent or more gallium were unusable.

Some further optimisation of the casting and mechanical properties was required and a series of ternary alloys based on the gallium-platinum system was evaluated; several combinations appeared to show a reasonable melting range while retaining good ductility, the relevant figures being given in Table IV. Small scale centrifugal casting trials using a fine claw setting dress ring pattern provided a critical test of fluidity and general casting characteristics, and revealed the good casting qualities of the solid solution gold-gallium-platinum alloys. Larger scale trials using production equipment determined the minimum casting temperature required to fill a standard production flask consisting of a button of six dress rings. In these the 3 per

cent gold-2 per cent gallium-platinum, the structure of which is shown in Figure 6, could be successfully cast at a lower temperature than alloys containing 2.5 or 3 per cent gallium despite having the higher melting

Fig. 6 The single phase microstructure of 3 per cent gold-2 per cent gallium-platinum shows some coring and fine interdendritic porosity. This alloy is also a suitable replacement for the 4.5 per cent copper-platinum alloy at present used for investment casting and has a significantly lower casting temperature



Alloy composition weight per cent	Casting temperature in air °C	Filling of a 6 dress ring casting button
4.5 Cu-Pt	2050	Complete
3 Ga-Pt	1960	Incomplete
2.5 Au-2.5 Ga-Pt	1990	Complete
3 Au-2 Ga-Pt	1960	Complete

Alloy composition weight per cent	Atmosphere during melting	Oxygen content of castings, ppm
3 Ga-Pt	Air	70
3 Ga-Pt	10% hydrogen/nitrogen	12
2.5 Au-2.5 Ga-Pt	Air	26
2.5 Au-2.5 Ga-Pt	10% hydrogen/nitrogen	14
3 Au-2 Ga-Pt	Air	18
3 Au-2 Ga-Pt	10% hydrogen/nitrogen	8

range. The results are given in Table V, together with comparable data for 4.5 per cent copper-platinum. This suggested that the gallium-containing alloys were susceptible to the absorption of oxygen, with a consequent reduction in fluidity. Further trials, in which the melt was protected by a reducing atmosphere, showed a significant improvement in the fluidity of these alloys thus enabling the

promoting metal-mould reaction, and any casting scrap could be re-cast providing 25 per cent virgin alloy, containing the deoxidiser, was added to each charge. While a small gain in alloy fluidity could be obtained when a deoxidant such as calcium boride was added to the melt prior to casting, the associated metal-mould interaction was considerable and made the castings unacceptable.

casting temperature required to fill the six-ring button to be reduced to about 1900°C. Gas analysis of the castings produced showed a significant decrease in the oxygen content when a reducing atmosphere of 10 per cent hydrogen/nitrogen had been used to protect the melt; the results are given in Table VI.

As an alternative approach the effects of adding a deoxidant to the alloy at the make-up stage or to the melt prior to casting, were evaluated. A small addition of yttrium incorporated in the alloy was found to be very effective in increasing alloy fluidity without

Alloy composition weight per cent	Atmosphere during melting	Minimum casting temperature °C
4.5 Cu-Pt	Air	2050
3 Au-2 Ga-Pt	Air	1960
3 Au-2 Ga-Pt+0.1 yttrium	Air	1930
3 Au-2 Ga-Pt	10% hydrogen/nitrogen	~1900

Table VIII
Comparison of Some Mechanical Properties of Existing and New Alloys in the As-Cast State

Alloy composition weight per cent	Density g/cm ³	Hardness H _v	Ultimate tensile strength MN/m ²	0.1% Proof stress MN/m ²	Elongation per cent
4.5 Cu-Pt	20.0	108	318	190	20.0
4.5 Co-Pt	20.1	134	400	182	20.0
3 Ga-Pt	19.8	153	262	139	17.0
2.5 Au-2.5 Ga-Pt	20.0	171	285	182	18.5
3 Au-2 Ga-Pt	20.3	134	346	162	19.6

To summarise, 3 per cent gold-2 per cent gallium-platinum can offer an advantage in casting temperature of between 90 and 150°C, depending on casting conditions, over the existing casting alloy, see Table VII.

Practical Evaluations

A comparison of the mechanical properties of the 4.5 per cent copper-platinum alloy, the 4.5 per cent cobalt-platinum and these lower temperature casting materials, which are given in Table VIII, suggests that the 4.5 per cent cobalt-platinum and the 3 per cent gold-2 per cent gallium alloys are similar to the 4.5 per cent copper-platinum in most aspects. They should therefore be amenable to the finishing techniques that the manufacturing jeweller normally applies to cast items. This has now been confirmed by the results of extensive trials completed by an independent jeweller who examined the stone-setting, ring sizing, soldering and polishing characteristics of 4.5 per cent copper-platinum, 4.5 per cent ruthenium-platinum, 4.5 per cent cobalt-platinum and the three gallium-platinum based alloys.

His report firmly recommends the cobalt-platinum alloy which was found to be superior to both 4.5 per cent copper- and 4.5 per cent ruthenium-platinum, while the 3 per cent gold-2 per cent gallium-platinum was considered to be a fully acceptable replace-

ment for the 4.5 per cent copper-platinum. There are no practical reasons against the use of either of the other two gallium-bearing alloys where a harder alloy is required, although the casting advantage of these is clearly less.

Conclusions

The work reviewed in this paper has shown that the high temperature alloy 4.5 per cent cobalt-platinum is superior in all aspects to the existing 4.5 per cent copper-platinum alloy for investment casting. The versatility of this alloy for casting the whole range of patterns from fine filigree to heavy section items has been clearly demonstrated. This together with its amenability to all the usual fabricating and finishing operations applied to such castings gives the jeweller the opportunity to improve both the quality of his product and the efficiency of his manufacturing process.

A significant decrease in casting temperature has been achieved with the 3 per cent gold-2 per cent gallium-platinum alloy, although it has not been possible to produce a platinum alloy that can be cast at temperatures comparable with those used for gold alloys. The advantage of this lower casting temperature is likely to assume even greater importance if the anticipated improvement in investment durability is achieved.