CHRISTOPHER CORTI
COReGOLD TECHNOLOGY, READING, U.K.

Chris Corti has over 33 years experience in the precious metals industry with Johnson Matthey and World Gold Council. He has focused on jewellery materials and manufacturing technology at World Gold Council, giving seminars and publishing Gold Technology and Gold Bulletin journals and the series of gold jewellery handbooks in his role as Editor. He led the MJSA/WGC task force on defining white gold and has frequently presented at Santa Fe Symposia and JTF conferences on a range of topics. He also has promoted industrial applications for gold and co-edited a new book, *Gold: Science & Applications*, published in December 2009. He currently runs his own consultancy, COReGOLD Technology and consults for the Worshipful Company of Goldsmiths, London.

Gold is unique amongst the jewellery precious metals in having a colour – a warm, deep yellow colour. It is also unique in that conventional carat gold jewellery, unlike the other white precious metals, can be produced in a range of colours from red through pink or rose to several shades of yellow, to green and eventually to white simply by varying the amounts and ratios of the alloying metals.
More interestingly and not so well-known, it is also possible to produce carat gold jewellery in unusual colours such as purple, black, brown and blue. Gold jewellery with such colour effects is commercially available and becoming increasingly popular. It is also possible to obtain interesting colours in platinum and palladium jewellery.
Some of these exotic colours are obtained by alloying gold with certain other metals to produce special alloy structures known as intermetallic compounds. The other colours are obtained by forming oxides or patinas on the jewellery surface by chemical or thermal treatments, similar to those used to colour cast bronze sculptures, or by coating the surface with thin layers of other materials.
In the jewellery industry, there is some mystery in how such unusual colours are produced as there is not a ready source of information covering this topic. It is useful, therefore, to review the technologies involved in producing these special colours in precious metal jewellery and also to highlight other potential approaches to broaden the range of colours for jewellery (and watch) applications that may emerge in the future.

Blue, Black and Purple! The Special Colours of Gold and Other Precious Metals

INTRODUCTION

Gold is unique amongst the jewellery precious metals in having a colour – a warm, deep yellow colour. It is also unique in that conventional carat gold jewellery can be produced in a range of colours from red through pink or rose to several shades of yellow, to green and eventually to white simply by varying the amounts and ratios of the alloying metals, typically copper versus silver, zinc, nickel and palladium. This colour variation is well documented[1-3] and is illustrated in the well-known colour triangle, Figure 1, for gold-copper-silver alloys.

More interestingly and not so well-known, it is also possible to produce carat gold jewellery in special colours such as purple, black, brown and blue. Gold jewellery with such colour effects is commercially available and becoming increasingly popular. There are two approaches to achieving such unusual colours: Some of these exotic colours are intrinsic to the alloy and are obtained by alloying gold with certain other metals in fixed amounts to produce special alloy structures known as intermetallic compounds. Otherwise, such colours are obtained by forming oxides or patinas on the jewellery surface by chemical or thermal treatments, similar to those used to colour cast bronze sculptures, or by coating the surface with thin layers of other materials. Both approaches could be used with the 3 other precious metals – silver, palladium and platinum - but have not yet found commercial interest. Of course, it is possible to colour carat golds and the other precious metals by coating the surface selectively with glass enamels in a wide range of colours, but that is another, separate topic and will not be discussed in this paper.

In some parts of the industry, there is some confusion and ignorance in how such colours are produced. It is not easy to find a ready source of information covering this topic. It is useful, therefore, to review the technologies involved in producing these special colours and how they may be applied to jewellery.

Earlier papers, focussed solely on gold, have been presented by Rapson[3] and Cretu and van der Lingen[4] and Corti has presented earlier versions of this review[5,6]. In addition, some of the possible techniques for producing black gold colours have been reviewed by Faccenda[7].

In presenting this paper, the focus is naturally on gold but I will make reference to some special colours that can be obtained in the other precious metals and also highlight other potential approaches to broaden the range of colours for jewellery (and watch) applications that may emerge in the future.

INTRINSICALLY COLOURED ALLOYS: THE INTERMETALLIC COMPOUNDS

Many metals, including gold and platinum, when alloyed with certain other metals at a fixed composition, can form intermetallic compounds, some of which have intrinsic attractive colours. In simple terms, these are analogous to chemical compounds where the different chemical element atoms combine in fixed ratios to form a particular compound such as sodium chloride - NaCl. In the case of gold, we are familiar with the hardening caused in copper-rich carat golds of 18 and lower caratages, which results from the ordered intermetallic compounds, AuCu and AuCu3. Here the compounds are formed in the atom ratios of gold:copper of 1:1 and 1:3 respectively, i.e 50 atomic % gold : 50 at% copper and 25 at% gold : 75 at% copper. These intermetallics do not have unusual colours.

In some binary alloy systems, the intermetallic compound occurs at a defined fixed composition and in others, it can occur over a narrow range of composition. The former often obey the chemical valency laws, whilst the latter are known as electron compounds. In general, intermetallic compounds are thermodynamically very stable and tend to be very hard and intrinsically brittle phases; they are not malleable and cannot be fabricated into complex shapes by conventional working techniques. Thus, their use in jewellery manufacture is not straightforward.

THE COLOURED GOLD INTERMETALLICS

There are three gold intermetallic phases known to have attractive colours, each with the formula AuX_2 where X is the alloying metal. Of these, the most well known is the gold-aluminium compound, $AuAl_2$, which has an intense purple or violet colour. It is known as 'purple gold' or sometimes as 'amethyst gold'. It was first patented in the 1930s by Degussa[8,9].

The purple intermetallic phase, $AuAl_2$, (more strictly described[10] as Au_6Al_{11}) occurs at 32.9 – 33.9 atomic % gold, which is about 79 weight % gold – 21 wt% aluminium[11]. Thus, it is theoretically hallmarkable as 18 carat gold. Interestingly, it can be formed in the bonds of gold wires and aluminium pads in electronic device manufacture if subjected to temperatures in excess of 250°C, causing joint embrittlement and failure. In the electronics industry, this phenomenon is known as the purple plague and its formation is undesirable! The material has a high hardness of up to HV 334.

The other two coloured gold intermetallics are the gold-indium compound at 46 wt% gold, $AuIn_2$, which has a clear blue colour[4,12] and melts at 544°C, and the gold-gallium compound at 58.5 wt% gold, $AuGa_2$, which has a bluish hue[4,12]. These tend to be soft, with hardness values of HV<100. The addition of thorium and tin to purple $AuAl_2$ also results in a blue colour[9].

The reflectance curves for these 3 purple and blue intermetallics are shown in Figure 2, taken from reference 12. For $AuAl_2$, like pure gold, there is a strong reflectance at the red-yellow end of the spectrum but, unlike pure gold, there is also a strong rise in reflectance at the blue-violet end of the spectrum, which results in the reddish purple colour. For the indium and gallium intermetallics, the drop in the middle of the spectrum is less marked, particularly for the gallium compound, and the red end of the spectrum is less strong, hence the blue colouration.

The CieLab colour co-ordinates for these compounds have also been measured[4,13] and are plotted on the graph in Figure 3, taken from reference 4.

Other coloured gold intermetallics are recorded: Mark Grimwade[14] has noted old German literature, dating back many decades (to 1937) in which it is reported that in the gold-potassium system, two intermetallics are coloured: Au_4K (at 4.7% potassium) which is olive green and Au_2K (at 9% potassium) which is violet (purple), but is sensitive to the air and 'needle-like'. Also the gold-rubidium intermetallic, Au_2Rb is a deep green. These are unlikely to be practical for jewellery use.

Application to jewellery manufacture

1. ***Solid alloy:*** Solid pieces of the purple gold intermetallic single phase material can be made by vacuum melting gold and aluminium in the correct ratio and casting. As mentioned earlier, this material is brittle and will shatter if hit by a hammer or dropped on the floor; it cannot be mechanically worked in the traditional manner. Mintek in South Africa have demonstrated the use of purple gold that has been faceted into a pseudo-gem stone by milling[4] and then set into conventional carat gold jewellery.

   Other techniques for making purple gold include powder metallurgy: A Japanese patent[15] claims additions of 7-30% of cobalt, nickel or palladium powders to gold-aluminium powders, which are pressed and sintered, presumably to give two-phase microstructures. These give a purple gold material with satisfactory workability, it is claimed. A similar patent was granted to Singapore Polytechnic in 2000[16] and purple gold jewellery made under this patent is marketed by Aspial Corporation, Singapore (www.purplegold.com). In a newer Japanese patent[17], ornamental purple gold alloys comprising 70-85% gold, rest aluminium are vacuum melted and atomised to powder. This powder is pressed in a mould and sintered by electric discharge heating.

   Another approach is through bundling of aluminium-coated gold and gold-coated aluminium wires together and drawing them down to a composite wire. These are then subjected to a thermal diffusion treatment in a reducing atmosphere at 450-700°C. In this way, a fibrous wire of purple gold is produced, with some gold in a two-phase structure that is tough and flexible[20]. In another Japanese patent[19] by

Seiko, gold articles with a purple colour comprise $AuAl_2$ particles embedded in a conventional high-gold matrix of gold-copper-silver alloy.

2. ***Reducing brittleness:*** Some of these patents imply that it is possible to reduce the degree of brittleness and obtain some measure of workability in purple gold intermetallic materials that contain second, ductile phases, i.e. the compositions are non-stoichiometric. In another approach[20], the brittleness of $AuAl_2$ can be overcome by obtaining the material with a very fine grain size of below 50 microns, which can be achieved by hot working or quenching. In this patent[20], specific mention is made of the composition Au 34 at. % – Al 66 at. % and a ternary alloy, gold 31 at. % - copper 3 at. % - aluminium 66 at. %. What the effect on colour of some copper in the composition is not specified *(but see later in the section on new intermetallic colours).*

   Recently, Fischer-Bühner et al[21] have examined the fracture behaviour of purple and blue (gallium) gold intermetallics by additional alloying. Using a novel and simple technique for assessing fracture behaviour, they demonstrated that improved crack resistance can be achieved by a micro-alloying addition to the blue gold-gallium intermetallic; the nature of the microalloying addition is not disclosed. For purple gold, alloying with palladium at 2 and 4 wt% levels gave some improvement but at the expense of colour intensity. When these Pd-containing materials were also microalloyed, there was a significantly larger improvement. It is assumed that these alloys with improved fracture behaviour are at least two phase in microstructure, as with conventional micro-alloying of gold[22], hence the improved fracture behaviour. Other recent work by Wongpreedee[23] has shown that alloying purple gold intermetallic with silicon and cobalt results in a finer grain size after rapid solidification of 5 microns compared to 280 microns of traditional purple gold-aluminium intermetallic, resulting in a material with improved fracture behaviour.

3. ***Coatings:*** Simply depositing an aluminium layer onto a gold surface and doing a diffusion heat treatment to produce a purple gold coating is possible[18]. Gold intermetallic materials can be applied to a substrate, such as conventional carat gold, by thermal spraying in a gas jet. For purple gold, this involves use of molten gold-aluminium alloy powders, either alone or with gold and aluminium powder[24]. The molten alloy particles impact and stick to the substrate surface to give a purple gold decorative coating. Physical Vapour Deposition (PVD) techniques such as sputtering or evaporation of gold and aluminium can also be used to produce purple gold coatings. Jewellery with such purple gold coatings has been produced commercially.

   More recent work by Klotz[25] has examined the application of purple and blue intermetallics to carat gold, silver and 950 platinum substrates by various coating techniques, including electroplating, laser or torch cladding or by dipping into liquid gallium. As he notes, these intermetallics are brittle and also have low corrosion resistance. By electroplating alternate layers of gold and indium in the correct thickness ratio on carat gold and sterling silver, followed by diffusion annealing, a blue intermetallic layer was produced at the surface, in thicknesses up to 50 microns, using reasonable annealing times. For the coating of a silver substrate, the use of a diffusion barrier of either rhodium or nickel was recommended prior to electroplating.

   Cladding trials, using laser or gas torch to melt purple or blue gold (as rods and powder) into machined grooves in carat gold items, was not very successful due to reaction with the substrate metal. Purple gold has a high melting temperature, 1060°C, leading to strong interaction with the substrate and consequent destruction of the item geometry. It was possible to use the technique for blue golds, but only by careful control. Laser melting of blue gold into grooves in 950 platinum was achieved in part but with a poor surface and surface porosity. Again, there was interaction with the substrate that gave rise to a grey colour in places. Dipping of carat gold into liquid gallium to form blue gold at the surface, analogous to galvanising steel with zinc, proved difficult due to the need for surface cleanliness and the difficulty of wetting gold by gallium and so was not considered a viable technique.

4. ***Casting:*** In their study, Fischer-Bühner et al[21] and their project partners investigated casting coloured gold intermetallic jewellery by conventional investment casting and by casting them in bi-metal jewellery.

This latter is a 2 step process whereby the first part of the jewellery is cast in the higher melting alloy. The remaining part is injected as wax around the first part and the combination invested, the mould de-waxed and burnt-out and the lower melting part (the coloured intermetallic) is then cast into the mould cavity.

These studies showed that microalloyed blue (gallium) gold intermetallic, which has a low melting (liquidus) temperature of about 490°C, could be successfully cast, unlike normal blue gold, with good form-filling and without cracking, in several designs but not all designs were suitable. Cracking due to bending stresses in finishing operations was also a hazard. It was noted that a dark bluish oxide formed on the surface, but this could be pickled off. A partner company also demonstrated that solid 'bead' shapes could be cast in both purple and blue (indium) golds; vacuum casting was necessary to prevent oxidation and loss of colour.

Bi-metal casting of blue (gallium) gold with 14 ct yellow or white gold proved problematic in that mixing of the two metal alloys occurred and there was also oxidation at the interface. Some better success was achieved when a higher-melting palladium 14 ct white gold was used. The casting of purple gold (containing 4% Pd) and blue gold, both microalloyed versions, with 950 palladium was successful with good bonding and stability.

5. ***Colour intensity and stability:*** If a purple gold alloy is aluminium-rich (versus stoichiometric composition), then two phase alloys comprising dendrites of $AuAl_2$ and aluminium solid solution result. The purple colour is diluted towards that of aluminium. On the gold-rich side, the second phase that appears is another (colourless) intermetallic, AuAl. The presence of second phases will cause a deterioration of colour intensity, despite reduced brittleness. According to Hori[26], the purple colour is preserved down to 15% of aluminium. However, work by Leach & Garner[13] has shown that the purple colour is quickly lost as the composition deviates from stoichiometric, Figure 4. Fischer-Bühner notes that additions of palladium up to 4% to purple gold shifts the colour from a deep to a pale purple, confirmed by quantitative Cielab colour measurements by Klotz[25]. Klotz notes that additions of >2% of metals such as palladium, copper or silver to purple gold cause the colour to fade rapidly.

   He also notes that platinum additions (which also form coloured intermetallics with aluminium, gallium and indium) to blue (indium) gold results in a mixture of intermetallic phases and causes the colour to move towards the apricot (yellow-pink) colour of the $PtIn_2$ intermetallic. The precipitation of this $PtIn_2$ phase in blue gold, $AuIn_2$, causes grain refinement and reduced brittleness.

   Colour stability is also important. Purple gold tends to turn brown (tarnish) due to a high release of aluminium in sweat, as found in artificial sweat tests[25]. Palladium additions to purple gold tend to reduce metal release rates. The blue golds also have a high metal release and in the case of the gallium blue gold, the colour quickly changes to golden-brown, due to the high gold content remaining in the surface layer. However, no colour change for the indium blue gold was noted. Klotz concludes that transparent protective coatings are probably required for jewellery application to protect them from tarnishing and hence colour degradation.

As noted earlier, purple gold jewellery is commercially available. The use of the blue intermetallic gold compounds in commercial jewellery appears to be more limited. This is due to their very pale blue colour and relative softness (about HV 140), so tending to scratch easily[25].

OTHER PRECIOUS METAL INTERMETALLICS

Probably the best known of other precious metal intermetallic compounds is the platinum-aluminium compound, $PtAl_2$, which is a golden yellow and contains 78 wt% platinum. According to Cahn[27], the addition of some copper moves the colour to an orange-pink. He reports that both forms have been used for jewellery and Mintek in South Africa have marketed $PtAl_2$ with copper additions as a pseudo-gem stone under the trade name 'Platigem[28]. By varying the platinum, aluminium and copper ratios in the range 58-80% platinum, the colours range from dusty pink through a subtle orange to a rich yellow[29]. The gemstone buttons can be prepared by melting in inert atmospheres and then cabouchoned or facetted to shape, if desired. The facetted approach involves some polishing.

As with gold, platinum forms coloured intermetallics with gallium and indium: $PtGa_2$ and $PtIn_2$ intermetallics are also yellow ($PtIn_2$ is an apricot colour). Palladium forms a coloured intermetallic with indium, PdIn, which is red unless there is an excess of palladium, when it moves to yellow[27]. This is confirmed by Argarwal and Raykhtsaum[13], who report that the palladium-indium compound, PdIn, has a reddish copper-yellow colour and that deviations from stoichiometric composition result in a rapid loss of colour, in a manner similar to that shown for $AuAl_2$, Figure 4 (b). The addition of some silver to this compound causes a more yellow (less red) colour.

To date, these coloured intermetallics, including the Platigem materials, have not seen wide commercial application and there are no reported studies of their relevant properties. They will be intrinsically brittle. It is very possible that there are other coloured precious metal intermetallics, as yet not reported in the literature. Whether any of these will have attractive strong colours of interest for jewellery is open to question.

SPECIAL COLOURS ON PRECIOUS METAL SURFACES: OXIDES, PATINAS AND COATINGS

We are all familiar with the turquoise blue patination of copper on roofs of buildings, the various brown-black patinas that grow on bronze sculptures and the tarnishing of silver and low carat golds, where the surface is slowly blackened by the formation of complex silver-copper sulphides due to corrosion by sulphur-containing species[30]. All these are examples of natural patinas, i.e. coloured surface layers arising from chemical reaction of the environment (corrosion) with one or more metals of the objects. The first two are examples of corrosion reactions deliberately exploited for decorative effect whereas the tarnishing of silver and gold is considered detrimental rather than decorative.

It is, of course possible to create coloured patinas artificially by immersion of the objects in various chemicals[31, 32] and cast bronzes are frequently subject to such treatments. It is also possible to artificially generate oxide (or anodised) layers on aluminium, titanium and niobium jewellery[33] that are naturally coloured, or coloured due to optical interference effects or can be coloured by incorporation of dyes into the anodised layer.

Such techniques, and others such as electroplating, are also used for colouring surfaces of gold and other precious metal jewellery. Typical colours available on commercial gold jewellery include black, grey, brown and blue. There is a growing interest in jewellery that incorporates such colours but it must be emphasised that these colours are only skin deep and that scratching or wear will reveal the conventional precious metals underneath. Their use is allowed under marking and hallmarking laws, as long as the underlying metal conforms.

We will examine such technologies on a colour by colour basis:

Black – Grey Gold

As Faccenda has already discussed[7], there are several approaches to obtaining a black surface layer on carat gold jewellery:

- Electroplating of ‘black’ metals
- Oxidation of alloys to form stable black oxides
- Chemical vapour deposition (CVD) of amorphous carbon

To this list we should also add:

- Patination

1. ***Electroplating:*** Typically, a range of black surface effects can be achieved on carat gold and other precious metal jewellery by electroplating with so-called ‘black rhodium’ or ‘black ruthenium’. These are special baths formulated with black additives to produce a hard black rhodium or ruthenium electroplated layer of up to 0.5 microns thickness on the surface. A post-plating treatment is necessary to give colour stability and wear resistance. The colours range from grey to ‘anthracite’ black (deep black colour of hard coal). Hardness values typically range from HV230 - HV310, the hardness depending inversely on the amount of black in the coating. Wear resistance is claimed to be good. Details of the plating process are given in reference 7. It is possible to electroplate black gold coatings

but these were not considered stable over time. However, a proprietary black gold plating system has recently become commercially available, under the tradename, 'Neropal'[34]. In addition, black and grey gold electroplating systems based on gold-nickel baths are commercially available[35].

2. ***Oxidation:*** Whilst annealing of conventional carat golds in air will produce a black copper oxide layer, this is not physically stable or durable. Consequently, special gold alloys have been developed to produce good, stable black oxide layers. Many of these contain cobalt, which forms a dense black oxide when the gold alloy is subjected to an oxidation treatment. This is done on the finished article; the black oxide can be subsequently polished by buffing to produce a quality finish. Alloys of gold with nickel or iron additions are also claimed to give grey-black oxides.

   A patent by Tanaka KKK in Japan[36] claims cobalt-containing alloys that form lustrous black cobalt oxide layers 0.1-10 microns thick. This patent is also applicable to platinum and silver alloys. In US patent 5,139,739, Takayanagi et al[37] claim gold alloys that contain at least one metal from the group copper, iron, cobalt and titanium, and also possibly one from the group comprising the 6 platinum group metals, silver and nickel. In their examples, cobalt and iron are the major additions to a range of 10,14 & 18 ct golds, each typically in the range of 5-20%. Oxidation is carried out in air at 700-950°C for times of about 20-60 minutes. Some commercial Japanese jewellery made under this patent is shown in Figure 5.

   Improved wear resistance of black gold can be obtained on 18 carat golds made from cobalt containing alloys through chromium additions[38] and the use of an electrolytic hardening cycle. The addition of chromium results in thinner oxide layers, comprising mostly chromium oxide, Cr_2O_3, which have an olive-green hue. The oxide on an 18ct 15% cobalt- 10% chromium alloy had better wear resistance than that on an 18 ct-25% cobalt alloy[4].

3. ***Amorphous carbon by CVD:*** The deposition of hydrogenated amorphous carbon layers on gold by plasma-assisted chemical vapour deposition for watch applications has been discussed by Faccenda[7]. This process operates at 200-400°C and produces a hard black coating, 1.0 – 1.5 microns thick, with good resistance to wear and impact and with an appearance of Chinese Lacquer. The hardness of this layer is very high, about HV 1800 – HV2000. It can also be applied to other jewellery metals as well as gold. Wear tests showed this coating to be superior to electrodeposited black ruthenium.

4. ***Patination:*** The application of chemical treatments containing oxygen and sulphur compounds can result in black and other colours on carat golds, generally through reaction with the copper in the alloy[31]. The oldest technique consists of immersing the items in impure potassium sulphide salts, known as 'Liver of Sulphur'. Other liquid sulphides and polysulphides are also used, preferably in diluted form to allow the films to build up more slowly but denser and more permanent. Untracht[31] suggests immersing the carat gold hot to produce a black colour or to use additions of 'aqua ammonia' (ammonium hydroxide) in the solution at room temperature. Immersion in barium sulphide solutions will produce a bluish-black colouration.

Brown Gold

Chocolate brown gold jewellery has been marketed in recent years as the latest fashion trend. Like black gold, this colouration is formed by a surface layer. The method used is not disclosed but is probably brown zirconium nitride deposited by Physical Vapour Deposition (PVD)[39]. Patination by immersion in Liver of Sulphur is another method discussed by Untracht[31].

Oxidation of gold alloys is achieved on special gold alloys. Brown oxides can be obtained with metals such as iron, manganese, nickel and copper, so that incorporating these metals into carat golds and oxidising them under controlled conditions produces brown oxides on the surface. Bright brown colours, based on this approach, are claimed in a Japanese patent[40] by Takayanagi of AIST for gold – silver (< 30% Ag) or gold-nickel-manganese (<30% Ni & 5-40% Mn) alloys containing 60-95% gold. The thickness of the brown layer and the degree of brownness increases with time of oxidation.

Blue Gold
Blue layers can be obtained by oxidation of carat golds containing special additions. Jewellery with such colour was launched in 1988 by VA Blue Gold SA of Switzerland[41], based on the patent by Muller[42]. In this, carat golds in the range 18-23 carats containing iron and a little nickel are oxidised at 450 – 600°C for 10-12 minutes. For an 18 carat alloy containing 24.4% iron and 0.6% nickel, a blue-green colour is obtained whereas for a 20 carat gold containing 14.4% iron and 0.6% nickel, a good blue colour is developed.

Kretchmer[42] has also developed blue gold jewellery that obtains its blue coloration from an optical interference effect on the oxide film. Gold alloys with 25% arsenic or iron are also known to produce blue colours. Friso et al[43] have shown recently that a 75% gold -23% iron-2% copper alloy forms a blue colour on oxidation at 400 – 500°C. When 2% chromium is added to this alloy, as well as a blue colour, an intense reddish-violet colour can be obtained at low oxidation temperatures.

In recent years, the jewellery company, Jarretiere, of Italy has marketed jewellery collections with blue gold, both bluish black and true blue colours, as well as black gold.

APPLICATION OF SPECIAL COLOURS IN JEWELLERY MANUFACTURE

As noted above, purple gold jewellery, based on the intermetallic gold aluminide, $AuAl_2$, is manufactured commercially. However, for designers and manufacturers wishing to incorporate this material in their designs, sourcing of purple gold from alloy suppliers is not easy. It is not a stock item generally. There are some alloy suppliers who will produce it on demand. It is also not easy to produce in-house, requiring vacuum melting and casting facilities. Its inherent brittleness also makes it difficult to process, as has been discussed earlier. Generally, it requires machining to shape by milling/grinding unless a powder metallurgy approach to near net-shape is taken (but beware patent infringement). Investment casting is also a limited (design) option. Care must be taken in polishing as imposed stresses can cause cracking. The same comments are true for the blue gold intermetallics. The inherent poor corrosion/tarnish resistance of these intermetallic materials is a drawback and the use of thin transparent protective coatings (similar to those developed for silver[54)]) has been suggested.

Black, brown and blue gold jewellery is also commercially available, made by oxidation treatments of special carat gold alloy compositions. Again, for potential manufacturers, these alloys are not typically stocked by alloy suppliers but need to be made to order. Again, care not to infringe patents needs to be exercised. However, these alloys can be processed normally, but oxidation treatments do need to be carried out under controlled conditions to ensure colour consistency. The use of black, blue or red rhodium/ruthenium/gold electroplating, discussed in the next section, to provide special colours is relatively straightforward to those skilled in electroplating; such facilities are found in many jewellery manufacturers and the use of toll platers is another option for those who do not have them.

For silver, platinum and palladium jewellery, there has been a lack of interest in providing colour effects apart from bi-metal jewellery with gold, although gilding of silver with gold is a traditional technology, of course. However, there is no inherent reason why the black/blue/red rhodium/ruthenium electroplating technologies could not be applied. It may also be possible to develop special alloys for oxidation treatments too, as the Tanaka patent suggests[36]. The 950 platinum--cobalt alloy forms a blueish colouration on its surface, for example, that might be developed into an interesting colour effect. The surface laser ablation technology, discussed in the next section, is also a useful option for providing novel surface colours.

THE FUTURE: NEW COLOURS FOR JEWELLERY

It has been said that totally new special colours for gold and the other precious metals are unlikely to emerge. However, there is some evidence to the contrary. I present some observations and conjecture below. It is, of course, arguable whether such colours are desirable! There are some who believe that terms such as ‘black gold’ and ‘blue gold’ are misnomers and should not be used as the gold alloy itself is not intrinsically of these colours[43].

Green Gold
A recent patent[35] by Takayanagi of AIST, Japan concerns production of a green gold by a patination technique on copper-containing carat golds in the range 15-67.5% copper. This produces what is described as a thin 'verdigris' film on the surface. A number of chemical mixtures are described to produce the green patina, many involving copper salts. I am not aware that green gold jewellery produced by patination is yet commercially available, although conventional 'green' carat gold jewellery in gold-silver alloys is commercially produced(this is actually a yellow colour with a green hue, rather than a strong green colour).

Red Gold
As stated in the section on blue gold, Friso et al[43] have shown it is possible to get an intense reddish-violet colour on the alloy surface through low temperature oxidation of a 18 carat gold-iron-copper- 2% chromium alloy. This is likely to be an optical interference effect rather than an intrinsic colour of the oxide.

Coloured electroplating systems: Blue and red rhodium
Recently, blue and red rhodium electroplating systems have been developed[46,47], analogous to black rhodium, although their application to carat gold jewellery has not yet materialised. Presumably, the blue and red colours are obtained with coloured additives to the bath, like the black version. Abrasion-resistant coatings of black, blue or red rhodium, up to 0.3 microns thick and with a gloss, can be plated in 30-90 seconds, it is claimed[37]. They can be put on gold, silver and nickel.

Colours through Boronising Treatments
In their paper presented at the 1984 IPMI conference, Matsuda and co-workers[48] studied the surface hardening of gold alloys by boronising treatments. The gold alloy is immersed in boron powder and subjected to thermal treatments at 900-950°C (1650- 1740°F) for about 6 hours. It was found that pure gold does not respond to boronising treatments but the alloying metals in gold alloys do react. Interestingly, in additional experiments, some binary alloys of gold with up to 15% of alloying addition were rolled to sheet and boronised at 850°C for up to 48 hours. This showed that some alloys produced layers with marked colours, as shown in Table 1.

TABLE 1: Colours produced on boronised gold alloys (up to 15% alloying addition)[48]

Alloy	**Colour**
Gold – lanthanum Gold - cerium Gold – neodymium	Purple-blue or blue
Gold – holmium	Deep grey
Gold – beryllium	Red – purple
Gold – manganese	Yellowish – brown
Gold – yttrium	No change

This is an interesting observation that suggests an alternative approach to surface colouration of gold alloys. As far as the author knows, this work has not been followed up. As well as sulphides and borides, possibly other compounds such as nitrides, selenides and silicides could be fruitful avenues of exploration? After all, titanium nitride is gold-coloured!

New intermetallic colours
As noted earlier, the three coloured intermetallic compounds of gold are binary alloys. Argarwal and Raykhtsaum[13] noted that silver additions to purple $AuAl_2$ shifted the colour towards yellow and the Degussa patent[9] notes that additions of thorium and tin shift the colour to blue whilst palladium additions shifts the colour to a pale purple [21,25.] Recent, unpublished work by Friso et al[43] on a 75 wt.% gold – aluminium- copper alloy indicates that increasing copper to 10 wt.% moves the colour to a pink, less intense hue.

For the indium blue phase, $AuIn_2$, additions of platinum shift the colour to apricot yellow. It can be presumed that other metal additions may have a different effect for all 3 intermetallic compounds. In the case of platinum, Cahn[27] noted that additions of copper to $PtAl_2$ shifted the yellow colour to an orange-pink. Again, these observations do not appear to have been pursued further, with the exception of the Platigem range of 'gemstones' developed by Mintek. They do suggest that ternary or higher order intermetallic alloys could yield new colours, analogous to shifting band-gap colour pigments such as the cadmium sulphides, used in plastics and ceramic enamels.

Colloidal gold colours

Ruby red glass is coloured by colloidal suspensions of gold nanoparticles. The same effect is used for purple-red to pink decorative glass enamel for tableware and glass. Colloidal gold, known as 'Purple of Cassius', is an ancient technology[49]. Colloidal silver is yellow and alloys of colloidal gold and silver are used in decorative glass enamels to shift the purple colour towards pink. Varying the nanoparticle size can shift the colour towards blue. As well as colouring glass and tableware, such nanoparticulate gold colours are being developed for colouring wool[50], paint and plastics[51].

In the current exciting world of nanotechnology research, nanoshells are an interesting development. They consist of a metal such as gold coated onto a dielectric core such as silica. These absorb light and so have a characteristic colour that depends on the relative metal thickness:core size. The colour is produced by a plasmon resonance mechanism. When the gold shells are made thinner, the purple colour shifts to greens and blues. Maybe, this effect could be used to create some novel glass enamels for jewellery use? Use of platinum and other precious metal nanoshells might also yield some interesting colour effects.

Surface Laser Ablation

Recent research at the University of Rochester, USA, has shown that use of laser ablation on metal surfaces can lead to a black colour[52] on metals such as gold and platinum through nanoscale roughening of the surface. This may be an alternative approach to obtaining a black colour on precious metal jewellery and offers the scope to make interesting decorative patterns. Not only that, but by varying processing conditions, other colours can be produced such as gold-coloured platinum[53].

CONCLUSIONS

I have attempted to demonstrate that gold jewellery can be made with some special colour effects, either due to intrinsically coloured intermetallic phases or to surface layers grown by reaction with alloying metals or by deposition techniques. A wide range of colours such as blue, black, brown and purple can be achieved and a number of techniques employed. However, there are some drawbacks: intermetallic colours are intrinsically brittle and surface coatings by any technique are liable to be fragile and will scratch and spall if knocked and wear away if rubbed constantly. Commercial jewellery in some of these special colours is available in the market.

I have also indicated that other precious metal jewellery such as platinum and silver can also be coloured by the same techniques, although the total range may not be as impressive as with gold.

Lastly, I have tried to spell out the scope for new colour effects and the possible technical approaches to develop them. The challenge is to develop them to commercial reality.

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Figure captions

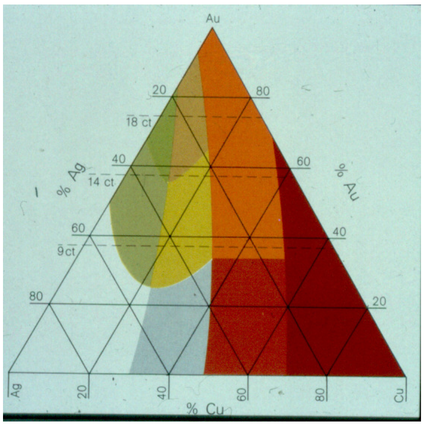
Figure 1 The Colour of Gold-Copper-Silver Alloys

Figure 2 Reflectivity curves for 3 gold intermetallic compounds (from Saeger & Rodies[12]): Curve 1 – $AuAl_2$, Curve 2 – $AuIn_2$, Curve 3 – $AuGa_2$

Figure 3 CIELab co-ordinates of coloured gold alloys (from Cretu & van der Lingen[4])

Figure 4 Effect of deviation from stoichiometric composition on CIELab co-ordinates for (a) $AuAl_2$ and (b) PdIn intermetallics (from Agarwal and Raykhtsaum[13])

Figure 5 Black gold jewellery, courtesy Seki Co and Mitsubishi Materials Corp, Japan



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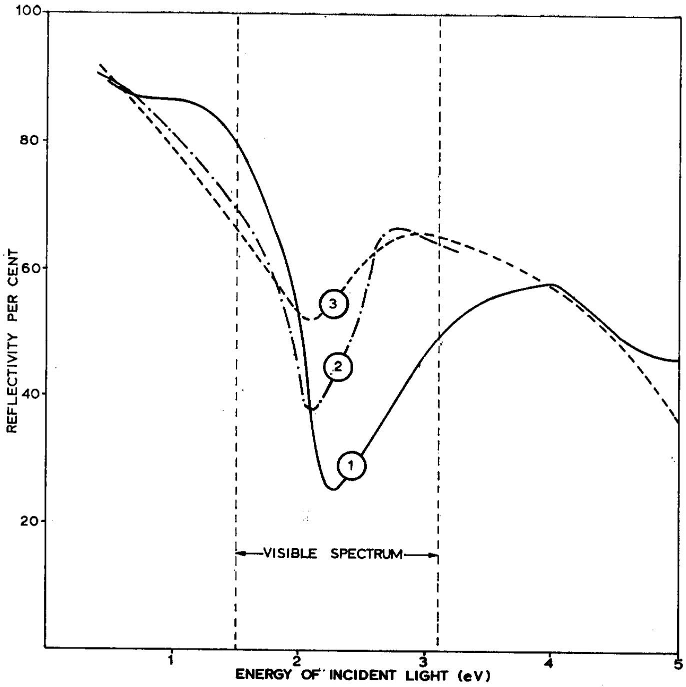

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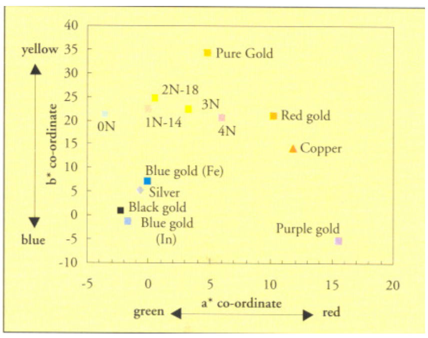

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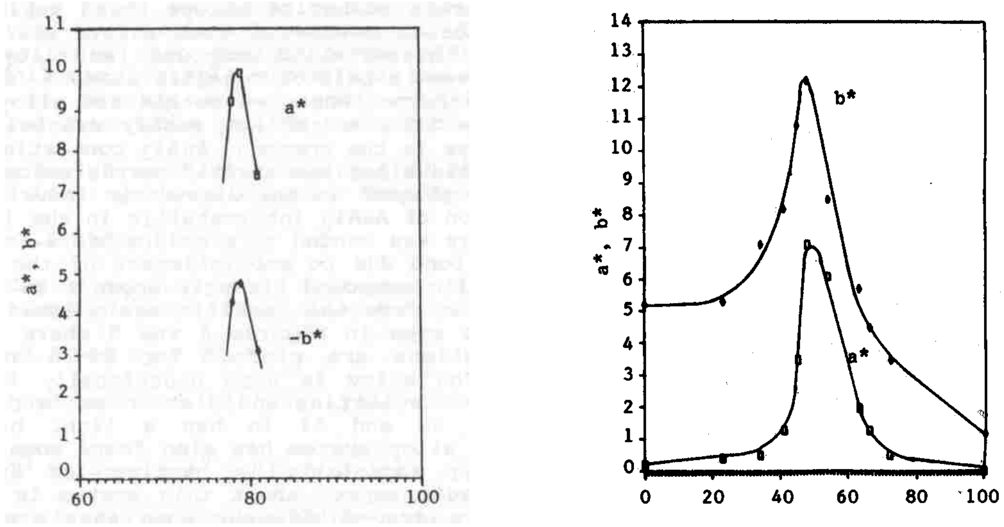

(a) (b)

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