

# "Purple glory": The optical properties and technology of AuAl<sub>2</sub> coatings

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## Abstract

The application of thin coatings of the purple gold intermetallic compound AuAl<sub>2</sub> provides a possible alternative to the use of this material in the bulk form. Here we explore the properties of AuAl<sub>2</sub> coatings prepared by vacuum deposition onto heated substrates. Control of the thickness and microstructure of the deposit allowed the optical properties of the film to be tuned over a wide range. The properties were characterised using CIE LAB colour coordinates, and by measurement and calculation of reflection and transmission spectra. Reflection colours could be varied at will between dark-silver through to light purple, and were largely a function of the degree of crystallization of the deposit. Transmission colours could be varied from light to dark greenish-brown, and were a function of both microstructure and film thickness. The complex refractive indices,  $n(\lambda) + i.k(\lambda)$ , and  $\epsilon_1(\lambda) + i\epsilon_2(\lambda)$ , of AuAl<sub>2</sub> were determined from the experimental measurements and are provided in tabular form. Proof-of-concept jewellery items were successfully produced to showcase the decorative aspects of this technology. Finally the possibility of using AuAl<sub>2</sub> as a spectrally selective coating on architectural glass was considered. Use of it would certainly provide a degree of solar screening with a somewhat more neutral colour than elemental Au coatings, but the figure-of-merit,  $T_{vis}/T_{solar}$  for the pure Au film is always better when compared at the same luminance.

## Introduction

The purple gold intermetallic compound AuAl<sub>2</sub> was discovered by W.C. Roberts-Austen [1] in 1892, and has been the subject of intermittent scientific and commercial interest since then [2-5]. The name 'purple glory' for this material was suggested by the late Robert Cahn in 1998 [3] but it is also sometimes known as 'amethyst gold' [6], or most commonly, just as 'purple gold'. While the deep metallic violet colour and 18 carat status of this material are attractive to the manufacturers of jewellery, its application has generally been confounded by its brittle nature. Actually, this problem is intrinsic to almost any intermetallic compound and has, for example, impeded attempts to apply the aluminides Ni<sub>3</sub>Al, NiAl or TiAl as jet engine turbines or compressor disks. This problem can be overcome in some applications by applying the compound onto a substrate as a thin coating, a possibility which we elaborate in the present paper. It is encouraging, for example, to note that the compound PtAl<sub>2</sub>, which has the same crystal structure and intrinsic brittleness as AuAl<sub>2</sub>, is applied commercially as a barrier coating on turbine blades of many jet engines.

It is helpful to first consider the nature of an intermetallic compound in order that the properties of AuAl<sub>2</sub>, and the other coloured precious metal intermetallic compounds, can be understood. Intermetallic compounds are formed when two or more metallic elements chemically combine in definite proportions to form a new phase. The new phase has a different crystal structure to that of the constituent metals and its properties are usually quite dissimilar to those of the elements from which it is comprised. These compounds typically have bonding that is intermediate in nature between metallic and covalent. Many of them possess attractive fundamental properties such as high hardness, high wear resistance, and good resistance to oxidation, although they are almost invariably associated with low toughness and low ductility. There has been considerable interest in using these substances in various high performance applications requiring, for example, strength at high temperature, specific magnetic properties, hydrogen storage, superior hardness and wear resistance, resistance to corrosion, thermoelectric and other specialized electronic properties, superconductivity and the shape memory effect [7].

Since intermetallic compounds are distinct phases with their own unique crystal structure and electronic configuration, they may also possess unique optical properties. Most are silver or silver-grey in the visible part of the spectrum but here and there, amongst the tens of thousands of possible candidates, are a few that display beautiful colours that are not found in the metallic elements or the simple alloys thereof. Historically, the earliest technological example is  $\beta$ -bronze [8], an electron compound with the stoichiometry Cu<sub>5</sub>Sn, which is a light golden yellow. Other intermetallic compounds with strong

colours include  $\text{AuAl}_2$ , the subject of this paper, as well as  $\text{CoAl}$ ,  $\text{CoGa}$  and  $\text{PtAl}_2$ , which are yellow,  $\text{AuGa}_2$  and  $\text{AuIn}_2$ , which are blue, and  $\text{CoSi}_2$  and  $\text{NiSi}_2$ , which are blue-black and blue-gray respectively [9]. In some systems a range of stoichiometry is possible, and the colour changes as the composition of those intermetallic compounds changes. For example in the  $\text{NiAl}$  system,  $\text{Ni}_{50}\text{Al}_{50}$  is light silver blue, but if excess Ni is added to produce  $\text{Ni}_{60}\text{Al}_{40}$  the colour becomes more yellow [9]. A blue-green colour is obtained if either Ni is partially replaced by Cu, or Al partially substituted by Si. In addition, some coloured intermetallic compounds exist at high temperature and/or in quenched state such as  $\text{NiIn}$  (violet) and  $\text{PtIn}_2$  (yellow) [9]. Many of the coloured compounds, including  $\text{AuAl}_2$  and  $\text{PtAl}_2$ , have the  $\text{CaF}_2$  or cF12 (Pearson notation) crystal structure.

The early investigators of  $\text{AuAl}_2$  were intrigued by the fact that yellow gold (melting point  $1064^\circ\text{C}$ ) and silver-coloured aluminium (melting point  $660^\circ\text{C}$ ) combined to form a compound ( $\text{AuAl}_2$ ) that was brittle, purple and with a melting point ( $1060^\circ\text{C}$ ) that was much higher than that of the compositions on either side of it in the binary phase diagram. The colour of the compound is now known to be the result of the fact that its electronic band structure allows photo-induced electronic transitions at around 2.1 eV, which is roughly in the middle of the visible range of light. This makes the compound absorptive in the mid-visible and reflective elsewhere, giving it its purple colour [4].

Unfortunately,  $\text{AuAl}_2$  is quite brittle and is difficult to process by traditional techniques. Nevertheless, items of purple gold jewellery have been produced [2, 6, 9, 10] and, with care, the material can be investment cast and even hot swaged [11]. Refinement of the grain size by hot or cold working has been reported to improve the toughness [9] but is evidently difficult. However, various other techniques for fabricating artefacts have been found. For example, in South Africa vacuum arc melting is used to produce small buttons that can be faceted to make a gemstone-like inset [2, 3]. Items of this latter jewellery have shown excellent endurance in low abrasion applications such as earrings and brooches, but a gradual decolouration of the buttons has been noticed in rings. A powder metallurgical process is reportedly [6] being applied by a manufacturer [10] in Singapore, to produce jewellery items, and another is claimed in a Japanese patent [12]. Early powder metallurgy patents referred to blends of 7 to 30 wt% of cobalt, nickel or palladium powders with the gold-aluminium powder, followed by pressing and sintering. A decade later, this technique was further developed to use  $\text{AuAl}_2$  powder produced by atomization of a vacuum-melted combination of the elements [13]. Another, less well-known, technique to produce purple gold involves making a composite wire of aluminium-coated gold or gold-coated aluminium by a thermal diffusion treatment. This material is reportedly tough, flexible and purple [14].

It has also been claimed that additions of alloying elements can be made to improve the ductility of  $\text{AuAl}_2$ . For example, according to a Japanese patent [15], one way to overcome the brittle behaviour is to lower the gold component to 75 wt%, and the aluminium content to between 20-24 wt%, with the remainder of the alloy (0.5-5 wt%) made up of one or two additional elements selected from the group consisting of silicon, magnesium, copper, zinc or manganese. A United States patent [16], made a similar claim, suggesting that a material with 76-83.5 wt% gold and 16.5-21.5 wt% aluminium should also contain 0.5-4.0% palladium or 1.0-2.0 wt% nickel as additional elements. The colour is bleached somewhat by the additional elements, but is still basically purple.

Decorative surface coatings of  $\text{AuAl}_2$  are another interesting possibility.  $\text{AuAl}_2$  produced by either plasma spraying or chemical diffusion of Al into Au have been applied in an attempt to improve the brittleness of purple gold [6, 9]. However, it was evidently difficult to control these processes and a porous product was often obtained. Physical vapour deposition (PVD), either by sputtering or by evaporation, can also be used to produce coatings of purple gold [6, 9].

Actually, there is also interest in  $\text{AuAl}_2$  for reasons other than mere decoration. The compound has been used as a superconductor at low temperatures [17], a spectrally selective solar absorber (ref.2 in [18]), as a thin film in radiation sensing devices [19], a resistor for Josephson integrated circuits instead of  $\text{AuIn}_2$  [20], for its tribological properties [21], and as a base electrode in a junction of many low  $T_c$  materials [22]. It also serves as a very suitable precursor with which to prepare mesoporous gold catalysts, electrodes and optically absorptive films [23-26]. In a less favourable context, the gold-aluminium intermetallics have a deleterious effect when formed during wire bonding with Au wire onto Al contacts in microelectronics. All five intermetallic phases ( $\text{AuAl}_2$ ,  $\text{AuAl}$ ,  $\text{Au}_2\text{Al}$ ,  $\text{Au}_3\text{Al}_2$  and  $\text{Au}_4\text{Al}$ ) are brittle [27, 28] and will form between any Au/Al couple given a sufficiently long exposure at high temperature. If mechanical failure of such a couple occurs then the purple colour of  $\text{AuAl}_2$  is usually visible on the fracture surface, giving rise to the term 'purple plague' to describe this undesirable phenomenon. There has also been considerable fundamental research directed at the thermal, electrical, magnetic, high-field galvano-magnetic and optical properties of the cF12 binary intermetallic compounds [18, 29-33]. Metallic fluorite compounds such as  $\text{AuAl}_2$  have been studied using techniques such as X-ray diffraction [34-37], X-ray absorption spectroscopy, ultraviolet and photoemission spectroscopy [38, 39], Raman spectroscopy [40], angle-resolved photoemission spectroscopy (ARPES) [41], and optical characterization [19, 42, 43].

There are, however, many topics that the prior research has not yet addressed. For example, the PVD process itself

has been only thinly explored in respect of  $\text{AuAl}_2$  coatings. Questions that arise, and which we will answer here, include: what is the effect of substrate temperature on the formation of  $\text{AuAl}_2$ , what are the optical properties of metastable deposits of Au and Al, what is the gamut of possible colours and how attractive are the optical properties of these coatings for technological applications? Finally, a point that has never been considered before is whether  $\text{AuAl}_2$  could serve as an active material in the rapidly growing field of 'plasmonics'. We will show here that it too can manifest a plasmon resonance with visible light, although one that is not as well developed as that of pure gold or silver.

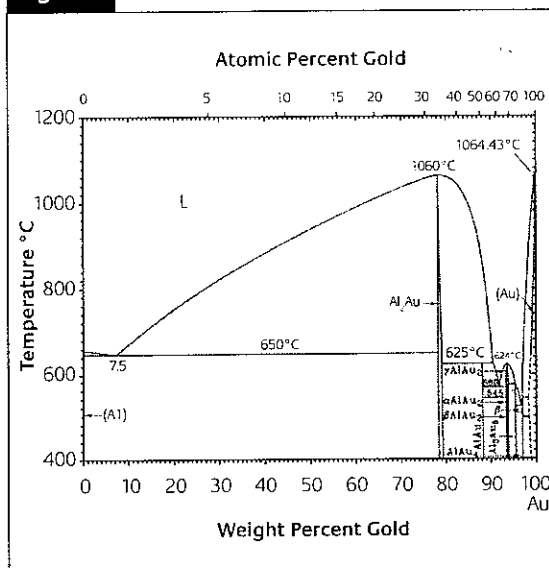
## Experimental

$\text{AuAl}_2$  films were prepared by PVD by co-depositing the elements using high vacuum, direct current magnetron sputtering. The films were either deposited onto glass substrates (soda-lime microscope slides) that had been cleaned with detergent solution for 20 minutes then rinsed with distilled water and dried with nitrogen gas, or onto metallic substrates that had been cleaned in ethanol and dried. The sputtering targets of Au and Al were 99.999% pure discs placed 150 mm away from the substrate. The base pressure of system was better than  $\sim 10^{-6}$  Torr ( $\sim 1 \times 10^{-4}$  Pa) while sputtering was carried out in the presence of flowing Ar at a pressure of 2.0 mTorr ( $\sim 0.3$  Pa). The sputter rates of elements were separately regulated for producing the desired stoichiometry and the rates of deposition calibrated using an *in situ* quartz microbalance sensor. The temperature of the sample during deposition was controlled by a substrate heater.

The purple phase is formed at about 79 wt% of gold and 21 wt% aluminium (33.9 at% gold), and has a very narrow composition range, as shown in the Al-Au binary phase diagram (Figure 1) [43]. In the present work the deposition parameters were adjusted until they gave the most intensely coloured film (purple in reflection and green in transmission), using both the human eye and the spectrophotometer as a guide.

Samples were normally heated to 400°C during deposition in order to expedite compound formation. Optical transmittance and reflectance of films were performed on a Perkin-Elmer Lambda 950 UV/VIS spectrophotometer. Optical properties parameters were obtained from the measured reflection and transmission spectra for the range 300 to 2500 nm using the WVASE32 program from J.A. Woollam Co., USA. The optimization calculations were run on an input file simultaneously containing data for both a 68 nm thick and a 100 nm thick film. Measured or calculated reflection or transmission spectra were converted to CIE LAB colour parameters using the appropriate standard methods [44]. Scanning

Figure 1



Al-Au phase diagram, reprinted with permission from ASM International® [43]

electron microscopy (SEM) with an energy dispersive spectrometer (EDS) was used to study the morphology and composition of the purple gold films. X ray diffraction was performed in grazing incidence mode using a copper tube.

## Results

### Reflection and transmission properties

The purple colour of  $\text{AuAl}_2$  on a glass substrate results from a reflectance minimum in the green region of the visible spectrum [4]. Figure 2 shows a plot of both the transmittance and reflectance for both experimental and modelled data for 68 and 100 nm thick films of  $\text{AuAl}_2$  produced in the present work by 8 and 17 minutes of deposition respectively.

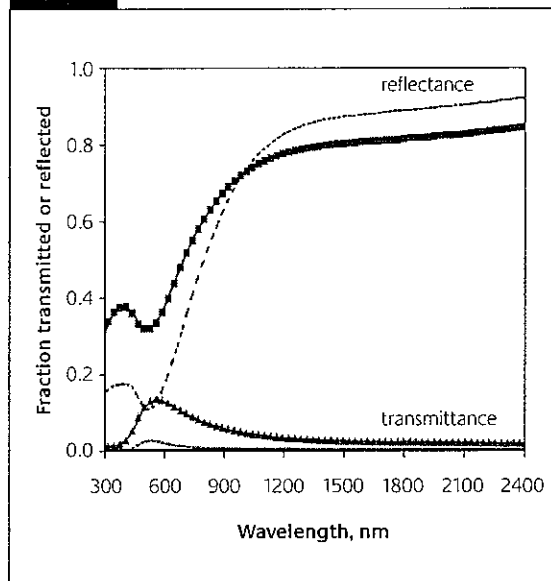
The complex refractive index and relative permittivity found by analysis of the data are graphed as a function of wavelength in Figure 3 and are also listed in Table 1 for convenience. Also shown (in Figure 3(b)) are the corresponding data for a gold film, made in the same laboratory and calculated the same way. The calculated and measured values of permittivity of the pure gold film are very close to the published literature values [45], providing confidence regarding the experimental and data-reduction techniques used in the present work. It can be seen that  $\epsilon_1$  in both cases can reach a value of  $\sim -2$ , in the case of pure gold at  $\sim 500$  nm and for  $\text{AuAl}_2$  at about 640 nm. This is very interesting, because plasmon resonance in a spherical nanoparticle will occur when  $\epsilon_1 \approx -2$ . Therefore, we predict that nanostructures of  $\text{AuAl}_2$  will also undergo

**Table 1**

Refractive index and permittivity of AuAl<sub>2</sub> film

Wavelength(nm)	n	k	$\epsilon_1$	$\epsilon_2$
300	2.058	1.499	1.988	6.167
330	2.084	1.722	1.378	7.177
360	2.042	1.863	0.700	7.610
390	1.842	1.872	-0.112	6.895
420	1.644	1.785	-0.485	5.869
450	1.430	1.639	-0.639	4.688
480	1.350	1.503	-0.439	4.057
510	1.289	1.406	-0.317	3.624
540	1.275	1.407	-0.353	3.586
570	1.235	1.470	-0.636	3.631
600	1.187	1.566	-1.042	3.719
630	1.117	1.717	-1.700	3.834
660	1.057	1.874	-2.393	3.961
690	1.007	2.042	-3.158	4.111
720	0.970	2.210	-3.942	4.288
750	0.944	2.372	-4.734	4.477
780	0.930	2.532	-5.546	4.711
810	0.921	2.686	-6.367	4.947
840	0.914	2.836	-7.207	5.187
870	0.907	2.985	-8.086	5.413
900	0.900	3.130	-8.985	5.633
930	0.899	3.273	-9.904	5.886
960	0.901	3.412	-10.830	6.147
990	0.905	3.548	-11.768	6.422
1020	0.919	3.682	-12.715	6.765
1050	0.936	3.814	-13.667	7.142
1080	0.953	3.946	-14.662	7.519
1110	0.971	4.075	-15.659	7.914
1140	0.993	4.201	-16.665	8.345
1170	1.020	4.325	-17.667	8.823
1200	1.049	4.446	-18.667	9.327
1230	1.077	4.562	-19.652	9.829
1260	1.107	4.676	-20.641	10.354
1290	1.141	4.789	-21.637	10.927
1320	1.178	4.898	-22.602	11.536

**Figure 2**



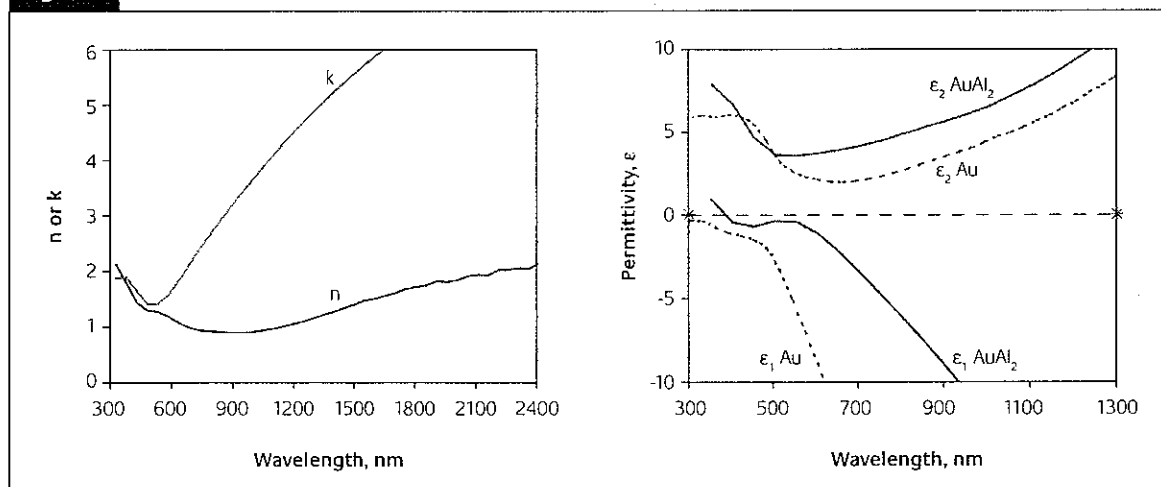
Transmittance and reflectance spectra of 68 nm thick AuAl<sub>2</sub> film with fitted model (solid line and symbols). Film was produced by 8 minutes of sputtering. Also shown, for comparison, is the reflectance and transmittance of a 100 nm thick film (dashed lines) produced by 17 minutes of sputtering.

plasmonic phenomena, a possibility which seems not to have been previously recognized. We will return to this point in the Discussion section.

#### Microstructure of coating

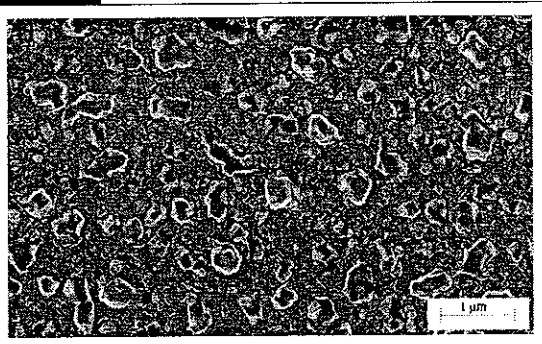
The surface morphology and composition of the AuAl<sub>2</sub> films were characterized using high resolution SEM and EDS analyses. The deposit exhibits a bimodal distribution of nanoscale crystallites (Figure 4). EDS analysis revealed that the Au and Al were present in an atomic ratio varying in the

**Figure 3**



Optical properties of AuAl<sub>2</sub> films as a function of wavelength, (a) complex refractive index, (b) complex permittivity. The data for films of pure gold is also shown in (b), for comparison

**Figure 4**



High magnification SEM image of 100 nm thick film of Au and Al co-deposited on glass substrate at 400°C

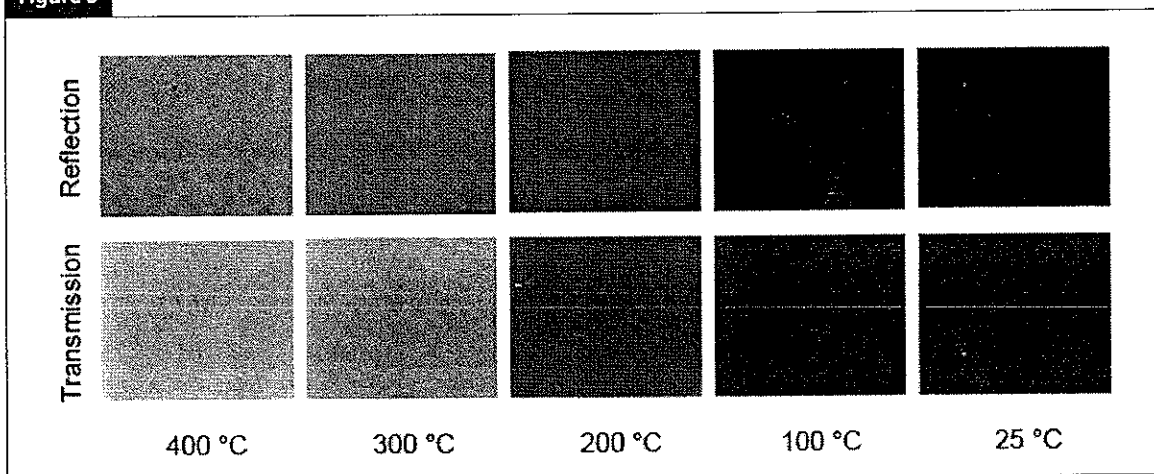
range 32:68 to 36:64. This is close to the 33.3:66.7 ratio expected for the  $\text{AuAl}_2$ .

The application of grazing incidence X-ray diffraction revealed that the coatings fabricated by co-deposition at 400°C consisted predominantly of well-crystallised  $\text{AuAl}_2$  (see Figure 7 later).

#### Effect of substrate temperature

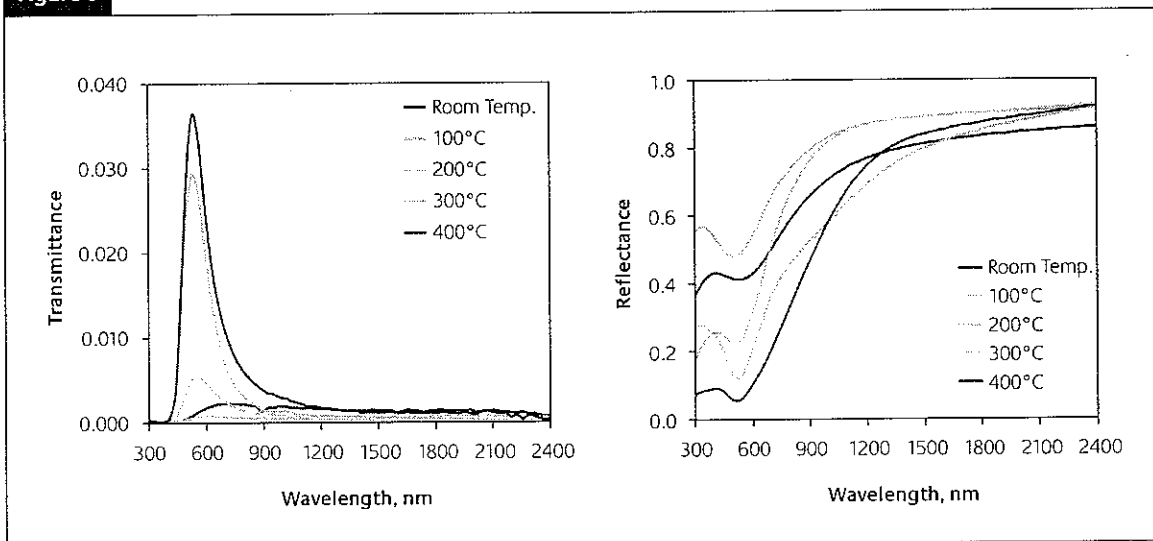
Prior experience had shown that the purple colour (and hence the  $\text{AuAl}_2$  compound) was not well developed during co-deposition of the elements unless the substrate was heated to about 400°C. Deposition at room temperature, for example, produced a silvery-grey coating. This phenomenon was investigated by systematically varying the substrate temperature, as shown in Figure 5. Figure 6 presents a plot of both the transmittance and reflectance after depositing at

**Figure 5**



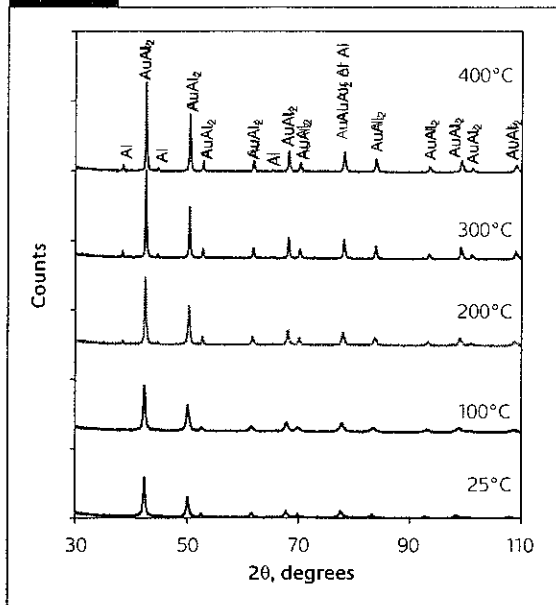
The colour of  $\text{AuAl}_2$  films with different annealing temperature in reflection and transmission

**Figure 6**



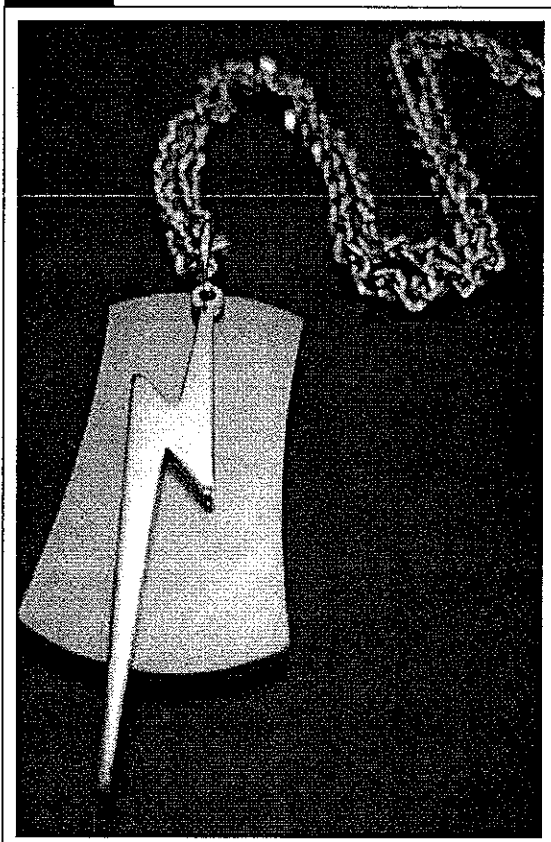
Transmittance and reflectance spectra of  $\text{AuAl}_2$  films with different annealing temperatures during deposition. Films were produced by 17 minutes of sputtering and are ~100 nm thick

**Figure 7**



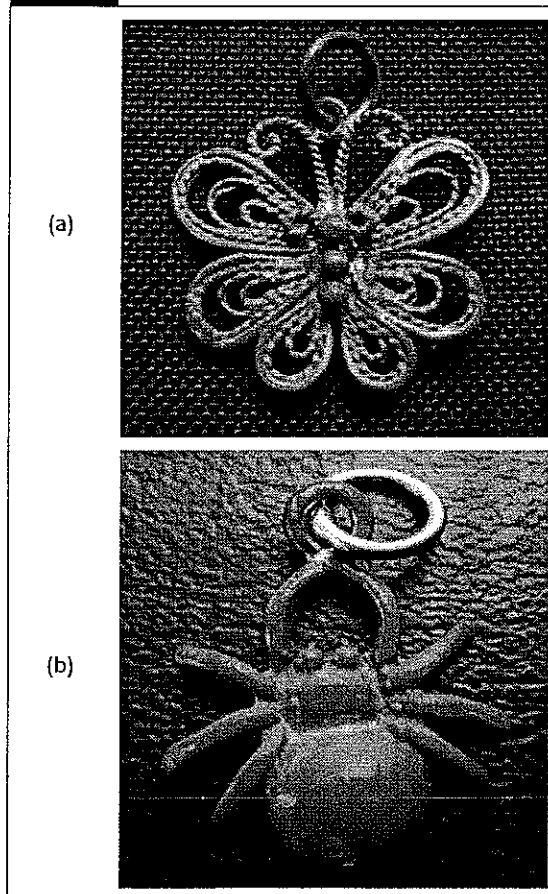
Series of X-ray diffraction patterns of  $\text{AuAl}_2$  on glass substrate produced with indicated substrate temperature during deposition

**Figure 8**



Prototype item of stainless steel costume jewellery onto which a film of  $\text{AuAl}_2$  of about 200 nm thickness has been applied for decorative effect

**Figure 9**



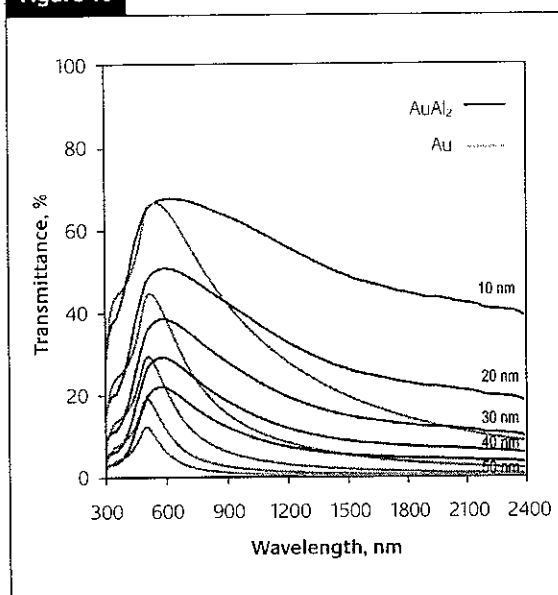
Items of experimental jewellery made by depositing an  $\text{AuAl}_2$  coating of approximately 200 nm thickness onto sterling silver costume jewellery. The deeper violet colour of the 'spider' is due to its substrate having been originally textured with a matt finish

different temperatures. X-ray scans of the resulting films are shown in Figure 7. It is clear that even the deposits made at room temperature do contain  $\text{AuAl}_2$ , but the broad and attenuated nature of the XRD peaks indicate that such material is either poorly crystallised, or present as exceedingly small grains. The XRD peaks become stronger, and sharper, as the substrate temperature is raised, indicating that the grains of  $\text{AuAl}_2$  are larger and/or more defect free when formed at successively higher temperatures. Evidently, the formation of crystallites of the  $\text{AuAl}_2$  phase requires a degree of mobility in the Au and Al atoms.

#### Application for jewellery

Purple gold was coated onto stainless steel (Figure 8) and sterling silver (Figure 9) costume jewellery as described above. In one case the sterling silver had a plain polished surface (Figure 9(a)), and in the other a textured surface (Figure 9(b)). The morphology of the surface evidently has an influence on the shade of violet produced.

Figure 10

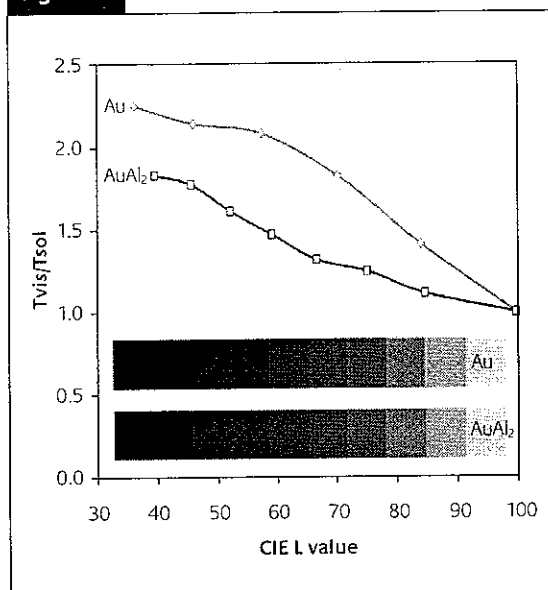


The prediction of transmittance spectra of Au and AuAl<sub>2</sub> films of different thicknesses

## Discussion

The optical properties of AuAl<sub>2</sub> bear a resemblance to those of gold, (Figure 3(b)) in so far as both materials have a negative  $\epsilon_1$  in the visible and near-infrared regions of the spectrum, and  $\epsilon_2$  values that decrease to a minimum in the mid or upper visible region. Therefore, the question of whether AuAl<sub>2</sub> might have any utility as a spectrally selective coating for windows has been raised, both during the present work and previously (ref. [2] in [18]). Of course, the amount of light transmitted depends on the thickness of the films applied. In Figure 10 we compare the predicted transmission spectra of Au and AuAl<sub>2</sub> coatings of a range of thicknesses, as applied to a clear glass substrate. It is clear that both materials tend to transmit more visible than infrared (a desirable attribute), but that the 'window' of transparency for plain gold coatings is narrower. Designers often use a figure of merit,  $T_{vis}/T_{sol}$ , to rank coatings, where  $T_{vis}$  or  $T_{sol}$  are respectively the fraction of light in the visible or total spectrum transmitted. A standard solar spectrum, the so-called Air Mass 1.5, is assumed in these simulations [46]. The  $T_{vis}/T_{sol}$  values of films of AuAl<sub>2</sub> and Au of different thicknesses are plotted in Figure 11. Also shown is the colour of the coating in transmission, determined by converting the transmission spectra into CIE LAB coordinates and then using one of the many CIE LAB to RGB conversions around to produce RGB colour tones for the purpose of the figure. We have plotted the colours of the coatings against CIE luminance, rather than coating thickness, since it is really luminance that matters in an application where the human eye is involved. Both the AuAl<sub>2</sub> and the Au coatings have good figures-of-

Figure 11



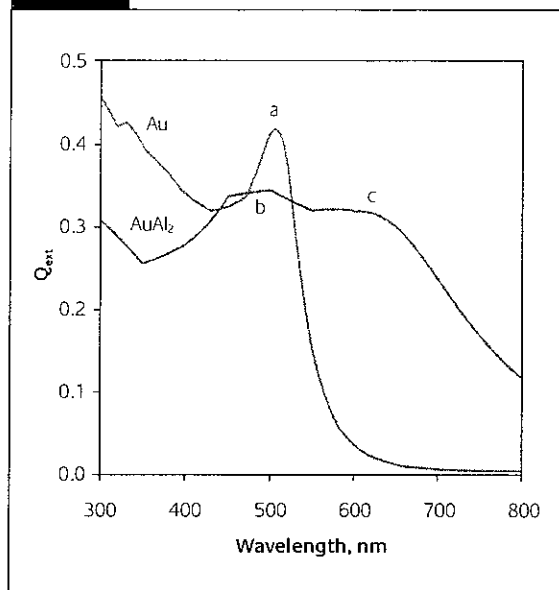
The calculated  $T_{vis}/T_{sol}$  values of films of AuAl<sub>2</sub> and Au of different luminances (derived by varying the thickness) and simulated colour of the resulting coating in transmission

merit, but those of the Au film are better at a given luminance. The gold films however, will have a far more pronounced greenish hue (in transmission) than those of AuAl<sub>2</sub>.

It is obvious from the foregoing that the colour of these coated systems depends on several factors, including the texture of the substrate, the thickness of the film and its degree of crystallinity. This provides quite a wide range of options for tuning the effect. Similarly, the CIE LAB parameters for AuAl<sub>2</sub> coatings has some variability. The CIE LAB colour coordinates for the reflected colour of well-developed films made in the present work by magnetron sputtering are in the range  $L=43$  to  $65$ ,  $a^*=6.8$  to  $15.6$ ,  $b^*=-2.2$  to  $-6.1$ , with the stronger colour produced by thicker films. In comparison the CIE LAB coefficients of bulk AuAl<sub>2</sub> have been reported in the range  $a^*=15.5$ ,  $b^*=-5$  [2]. The colour in transmission depends even more sensitively on the thickness of the film but for a 68 nm film values of  $L=41.3$ ,  $a^*=-5.0$ ,  $b^*=22.4$  were obtained.

It was mentioned that a value of  $\epsilon_1 = -2$  in a material is associated with a localised plasmon resonance phenomenon in nanoparticles. However, the phenomenon is also modulated by the value of  $\epsilon_2$  (the imaginary part of the dielectric properties) so the actual extent of the resonance is the result of an interplay between these factors. To investigate this we simulated the optical properties of nanospheres of Au and AuAl<sub>2</sub> using a program [47] that calculated the Mie scattering. Regrettably, the plasmon resonance in AuAl<sub>2</sub> nanoparticles seems to be highly attenuated and somewhat uninteresting compared to those of pure gold, Figure 12.

**Figure 12**



Calculated optical extinction spectra of 20 nm diameter nanospheres of Au and AuAl<sub>2</sub> in vacuum. The main effect of the localised plasmon resonance of Au spheres is to create a strong and narrow extinction peak centred on about 520 nm ('a'). The nanosphere of AuAl<sub>2</sub> is predicted to have a broad and overlapping pair of extinction peaks ('b' and 'c'), centred on about 480 and 600 nm

## Conclusion

High purity, continuous films of coloured intermetallic compounds of AuAl<sub>2</sub> can be fabricated by vacuum sputtering techniques. Control of the substrate temperature during deposition provides a useful means by which the crystallinity and optical properties of the coatings can be varied. These coatings can be applied to jewellery, and could be hallmarkable as 18 carat gold. The colour perceived by the human eye depends on the texture of the underlying surface, the degree to which the microstructure is crystallised and, in transmission mode, on the thickness of the film. The dielectric optical properties of AuAl<sub>2</sub> films were determined and are tabulated. The range of possible colours and other optical characteristics of films of different thicknesses was then investigated by a combination of measurement and calculation. Although AuAl<sub>2</sub> films do have reasonable spectral selectivity, they would not be competitive with gold in terms of selective attenuation of the infrared. On the other hand, the optical properties of these films can certainly be varied over a wide range by controlling the development of their microstructure.

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