Optical Properties of Au-Pt and Au-Pt-In Alloys

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The effects of platinum addition to gold and indium addition to a gold-platinum alloy on their optical properties were investigated using a computer-controlled spectrophotometer. Spectral reflectance data from a polished sample for the incident CIE standard illuminant D65 was collected as a function of the wavelength at 10 nm intervals from 360 to 740 nm. Three coordinates, *L^** (lightness), *a^** (red-green), *b^** (yellow-blue), in the CIE 1976 *$L^*a^*b^*$* colour space, were determined to quantify the colour of experimental binary Au-Pt and ternary Au-Pt-In alloys.

The pronounced step near 520 nm (approximately 2.4 eV) in the spectral reflectance-wavelength curve for pure gold, which is responsible for the rich yellow colour of gold, became less pronounced with the addition of platinum. The decoloring effect of platinum was found to be due to this phenomenon. The addition of indium of up to *ca* 4 at% to a Au-10 at% Pt alloy increased both chromaticity indices, *ie*, *a^** and *b^** values, giving a gold tinge to the alloy: this effect was brought about by both the slight increase in reflectance in the long-wavelength range and the slight decrease in reflectance in the short-wavelength range of the visible spectrum.

Gold-based alloys are widely used in dentistry for constructing various prosthetic appliances, such as inlay, crown, bridge, and porcelain-fused-to-metal restorations. The colour of a gold-based alloy is known to be sensitive to alloying elements and their contents. Recent development of a computerized spectrophotometer has led to quantitative analysis of the colour of metals and alloys. For traditional dental casting gold alloys, Roberts and Clarke (1) and German *et al* (2, 3) assessed the relationship between alloy colour and composition in the Au-Ag-Cu ternary system.

With regard to dental precious metal alloys for porcelain bonding, palladium-free gold alloys were developed in Europe and introduced into the market. These palladium-free alloys may be attractive for patients who are allergic or hypersensitive to palladium. Most of these gold alloys contain *ca* 10 at% platinum and a small amount of additives including indium. Although colour is one of the important criteria in developing and selecting dental gold-based alloys, a quantitative relationship between optical properties and composition in the Au-Pt-In system has not previously been assessed. The objectives of this research were to quantitatively analyse the effects of platinum addition to gold and the effects of indium addition to a Au-10 at% Pt alloy on their optical properties. A computerized spectrophotometer was employed to characterize the colour properties of the experimental alloys.

MATERIALS AND METHODS

Table 1 lists chemical compositions of the alloys examined. All the alloys were prepared from high-purity constituent metals using a high-frequency induction furnace. The ingot obtained was subjected to alternate cold rolling and homogenizing heat treatment at high temperatures. Square plate samples, 10 x 10 x 0.5 mm^3 in size, were the final products. Three square plate samples for each alloy were individually embedded in epoxy resin and mechanically ground using waterproof abrasive papers. After being ground to a 1500-grit finish the samples were polished with an alumina slurry using an automatic polishing apparatus (Doctor-Lap ML-180, Maruto Instrument Co, Ltd, Tokyo, Japan). The polished surface of a sample was rinsed with water and dried.

The samples were then placed on a computerized spectrophotometer (CM-3600d, Minolta Co, Ltd, Osaka, Japan) and subjected to colour measurements. The spectral reflectance data for the incident CIE (Commission Internationale de l'Eclairage) standard illuminant D65 were collected at 10 nm intervals from 360 to 740 nm. Three-dimensional coordinates, *ie*, L^* (lightness), a^* (red-green), b^* (yellow-blue), in the CIE 1976 $L^*a^*b^*$ (CIELAB) colour space were determined for each experimental alloy. The L^* values can range from 0 (black) to 100 (white). Positive a^* values

Table 1 *Chemical Composition of the Alloys Examined (Analysed Values)*

Alloy	Composition (at.%)		
	Au	Pt	In
AP5	95.1	4.9	0
AP10	90.1	9.9	0
AP10-In2	88.4	9.9	1.7
AP10-In4	86.5	9.6	3.9

correspond to red, and negative a* values correspond to green. Positive *b** values correspond to yellow, and negative *b** values correspond to blue. Three samples for each alloy were subjected to the colour measurements.

The colour difference, ΔE^*_{ab}, between two samples was evaluated by the distance between two points in the CIELAB colour space. The ΔE^*_{ab} value, each given in terms of L^*, a^*, and b^*, was calculated with the formula:

$$\Delta E^*_{ab} = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2} \quad (1)$$

where, ΔL^*, Δa^*, and Δb^* are differences in L^*, a^*, and b^* values, respectively, for the two samples.

RESULTS

Reflectance of Au, Pt, and Binary Au-Pt Alloys

Figure 1 shows spectral reflectance curves for pure gold, pure platinum, and the binary gold-platinum alloys containing *ca* 5 at% Pt (AP5) and 10 at% Pt (AP10). Reflectance by pure gold was high in the long-wavelength range, but very low in the short-wavelength range. As a result, a pronounced step in the reflectance curve occurred in the vicinity of 520 nm. For platinum, on the other hand, a fairly flat reflectance curve was observed in the whole range of wavelengths measured. It is noted that the reflectance of pure platinum was already low in the long-wavelength range and slightly decreased with decreasing wavelength.

Platinum addition to gold markedly changed the shape of the spectral reflectance curve. That is, the addition of only about 5 at% Pt to Au increased the reflectance in the short-wavelength range. The addition of about 10 at% Pt to Au further increased the reflectance in the short-wavelength region, but markedly decreased the reflectance in the long-wavelength region of the visible spectrum. As a result, the pronounced step in the reflectance curve, which is peculiar to gold, became less pronounced with increasing platinum content.

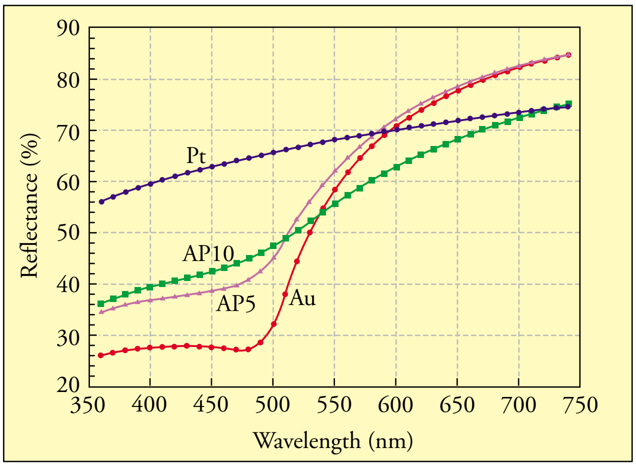

Figure 1 *Reflectance-wavelength curves for Au, Pt and binary Au-Pt alloys*

Reflectance of Ternary Au-Pt-In Alloys

Spectral reflectance data for the ternary Au-Pt-In alloys are presented in Figure 2. The spectral reflectance-wavelength curve for the binary AP10 alloy is also included as a reference. Alloying a small amount of indium to the parent Au-Pt alloy (AP10) appreciably increased the reflectance in the long-wavelength region, and lowered the reflectance in the short-wavelength region. This trend increased with increasing indium content. Consequently, the slope of the reflectance-wavelength curve near 520 nm became steeper with increasing indium content.

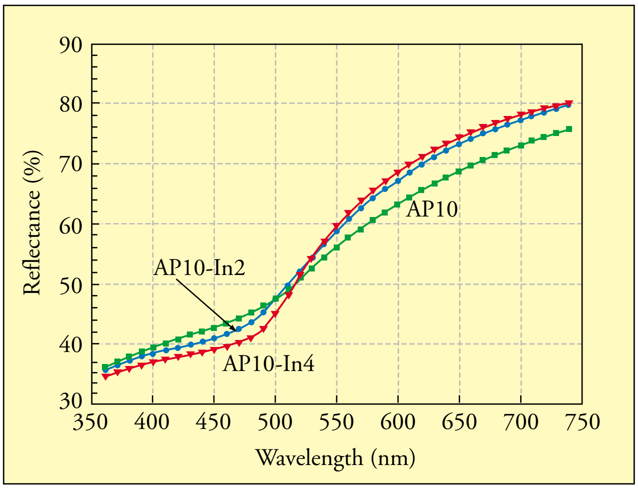

Figure 2 *Reflectance-wavelength curves for the AP10 and ternary Au-Pt-In alloys*

The CIELAB Colour Coordinates

Table 2 gives the CIELAB colour coordinates for the metals and alloys examined. The L^* values were high in all the samples and not affected much by the alloying additions. The a^* and b^* coordinates evaluated are plotted in Figure 3. It is seen that the addition of platinum to gold markedly decreased both chromaticity indices a^* and b^*.

The addition of a small amount of indium to the parent AP10 alloy appreciably increased both a^* and b^* values. As a result, the point for the ternary Au-Pt-In alloy moved towards the position for pure gold with increasing indium content, as indicated by arrows. This finding clearly indicates that the indium addition to the AP10 alloy gives a gold tinge to the alloy.

The CIELAB Colour Difference

The CIELAB colour differences, ΔE^*_{ab}, between the two experimental alloys were estimated according to the formula (1) and summarized in Table 3. All these figures were considerably larger than 1.0. Since ΔE^*_{ab} at 1.0 is just discernible by average human eyes (4), these results suggest that colour differences between any two experimental alloys can easily be distinguished.

Table 2 *CIELAB Colour Coordinates for the Metals and Alloys*

Metal/Alloy	L^*	a^*	b^*
Au	79.40 (0.09)	11.22 (0.07)	33.59 (0.20)
AP5	82.25 (0.28)	7.38 (0.06)	22.91 (0.10)
AP10	79.49 (0.22)	5.03 (0.08)	13.73 (0.05)
AP10-In2	80.80 (0.05)	5.93 (0.00)	17.65 (0.03)
AP10-In4	80.83 (0.28)	6.73 (0.03)	20.26 (0.32)
Pt	86.11 (0.05)	0.88 (0.00)	4.52 (0.03)

Average for three specimens with standard deviation in parenthesis

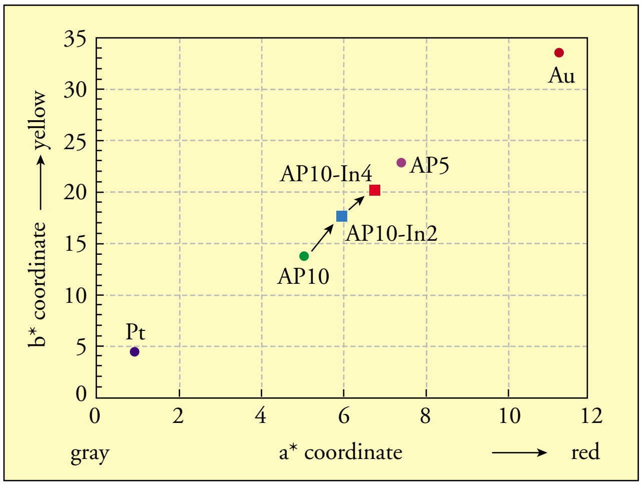

Figure 3 *Chromaticity indices a* and b* for all the metals and alloys examined*

DISCUSSION

Effects of Platinum Addition to Gold on its Optical Properties

The optical properties of a metallic material are related to the absorption and re-emission of photons of light. The perceived colour of metals is determined by the wavelength distribution of the reflected radiation (5). For instance, the rich yellow colour of gold arises from high reflectance in the yellow to red range and low reflectance in the purple to blue range of the visible spectrum. As a result, a pronounced step in the reflectance-wavelength curve is observed around 520 nm (approximately 2.4 eV), as seen in Figure 1. The intense absorption of light in the short-wavelength part of the visible spectrum for gold is known to be due to the transitions of electrons from a *d*-band to energetically higher unoccupied states above the Fermi level in the conduction band (6).

With transition metals such as Ni, Pd and Pt, absorption begins in the infrared range and is fairly

Table 3 *CIELAB Colour Difference, ΔE^*_{ab}, between Various Metals and Alloys*

Metal/Alloy	Au	AP5	AP10	AP10-In2	AP10-In4	Pt
Au	–	11.7	20.8	16.9	14.1	31.6
AP5	_	_	9.9	5.6	3.1	19.9
AP10	–	–	–	4.2	6.9	12.1
AP10-In2	–	–	–	–	2.7	15.0
AP10-In4	–	–	–	–	–	17.6
Pt	–	–	–	–	–	–

uniform in the visible spectrum (7). In fact, we observed relatively low reflectance in the long-wavelength range for pure platinum, as shown in Figure 1. Mott and Jones (7) suggested that the work required to remove an electron from a state in the *d*-band to an empty state in the *s*-band is very small in these transition metals and the absorption band is due to such transitions.

Alloying platinum to gold systematically increased the reflectance in the short-wavelength range and decreased the reflectance in the long-wavelength range of the visible spectrum, as seen in Figure 1. As a consequence, reflectance-wavelength curves for the binary Au-Pt alloys progressively flattened with increasing platinum content. It is clear that the flattening of the reflectance-wavelength curve due to platinum addition gave rise to the decolorizing effects. Friedel (8) suggested that when monovalent noble metals are alloyed with transition metals, so-called 'virtual bound states' would occur. In fact, Abelès (9) showed that the maxima of the relatively broad absorption peaks caused by the virtual bound states existed at energies of approximately 0.8 eV (approximately 1550 nm) for Au-Ni and 1.7 eV (approximately 730 nm) for Au-Pd systems. It may be reasonable to consider that the absorption process in the present Au-Pt system may also start in the infrared range due to the occurrence of virtual bound states as suggested by Friedel (8). This is based on our experimental evidence that the reflectance for pure platinum was already low in the long-wavelength range (Figure 1), and Abelè's work (9) on both the Au-Ni and Au-Pd systems. In addition, the fact that the step around 520 nm in the reflectance-wavelength curves became less pronounced with increasing platinum content suggests that the ejection of *d* electrons gradually weakened with increasing platinum content.

Effects of Indium Addition to a Gold-Platinum Alloy on its Optical Properties

Since optical properties of metals and alloys are determined by the interaction between the photons of the incident light and the electrons in the metallic material, the number of valence electrons per atom (*e/a*) in a metallic material may affect this absorption process. That is, the degree of absorption or reflection of light presumably becomes more intense with increasing *e/a* value. The numbers of valence electrons per atom in Au, Pt, and In, have been reported to be one (10, 11), zero (10, 12), and three (10, 11), respectively. Based on these reported *e/a* values for constituent metals and the chemical compositions in at%, we simply estimated the *e/a* values to be 0.901, 0.935, and 0.982 for the AP10, AP10-In2, and AP10-In4 alloys, respectively. Results of this estimation clearly indicate that the *e/a* value of the present ternary alloys increases considerably with increasing indium content. This effect of indium addition is considered to be the primary cause for giving an additional gold tinge to the Au-Pt-In alloys.

CONCLUSIONS

Effects of platinum addition to gold and indium addition to a Au-Pt alloy on their optical properties were investigated by spectrophotometric colorimetry. The following conclusions were drawn:

1. The rich yellow colour of gold was considerably weakened by the addition of about 10 at% Pt. This was due to the fact that the pronounced step around 520 nm in the reflectance-wavelength curve for pure gold became less pronounced with the addition of platinum.
2. The addition of a small amount of indium to a Au-Pt alloy effectively increased both chromaticity indices, *a** and *b**. This gave a useful gold tinge to the alloy.

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BOOK REVIEW

Cyanide: Social, Industrial and Economic Aspects

Ed by Courtney A Young, Larry G Tidwell and Corby G Anderson, The Minerals, Metals and Materials Society, Warrendale, Pa, USA, 2001, 582 pages, ISBN 0-87339-479-8, Price $120.00

This book collects together 43 papers which were presented at a conference with the above title. Following standard refereeing procedures the papers were published in the book under review and then the conference was held in New Orleans from 12 - 15 February 2001. The editors claim that all the desired subject matter was covered to some degree.

Cyanide management technologies have been greatly improved and new technologies are being implemented and developed, including analysis and control. An understanding of cyanide physico-chemical properties under different conditions (*eg* pH, redox potential, temperature, pressure) is essential for the safe measurement of cyanide.

Use of cyanide by the mining industry has become a target of some environmental groups and, for example, the State of Montana in the USA now prohibits use of cyanide for heap and vat leaching of gold and silver ores mined by open-pit methods. Active consideration is therefore being given to alternative reagents in order to gain public consent.

Most of the papers in this volume describe some aspect of cyanide technology, but there are others describing use of thiosulfate and other alternative lixiviants, *eg* halide and nitrogen species. There is certainly a wealth of information for readers wishing to assess the pros and cons of new approaches to the use of cyanide and alternatives.

The book is divided into the following sections: 'Politics and Spills' (10 papers), 'Analysis and Control' (6), 'Cyanide Management' (20), 'Alternatives' (7); and there is an Addendum containing three more cyanide papers, one of which is by Anglogold authors. There is an Author Index and a small but useful Subject Index.

David T Thompson