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#### Synopsis

This paper provides a review on coloured gold, platinum, and palladium intermetallic compounds, and discusses the models that were developed to obtain these materials. These compounds have a crystal structure of high symmetry, such as the CaF<sub>2</sub> or CsCl structures, ensuring distinct electron band structures. Various examples of coloured gold, platinum, and palladium intermetallic compounds are provided. More in-depth discussion is provided on the purple gold (AuAl<sub>2</sub>) and yellow platinum-aluminium (PtAl<sub>2</sub>) compounds with CaF<sub>2</sub> structure, as well as the purplish-pink palladium-indium (PdIn) compound with CsCl structure.

Precious metal intermetallic compounds are used in jewellery and provide a new dimension to design. Some of these compounds have also found use as barrier coatings on turbine blades for jet engines, and more recently, research has been conducted into their potential use as catalysts, electro-catalysts, sensors, capacitors, and for decorative coatings.

#### Keywords

colour, gold, platinum, palladium, intermetallic compounds, CaF $_2$  structure, CsCl structure, AuAl $_2$ , PtAl $_2$ , Pdln.

#### Introduction

Intermetallic compounds are compounds consisting of two or more metals in which the numbers of the atoms of the different metals are at, or near, a simple ratio e.g. PtAl<sub>2</sub>. In most cases, intermetallic compounds solidify at a fixed temperature and composition, and have thus a narrow domain of existence. The crystal structure of an intermetallic compound is normally different from those of the individual metals from which it is composed. Fundamental properties of intermetallic compounds are usually high brittleness with associated low toughness, high hardness, good wear resistance, and good corrosion resistance.

Only about 100 compounds among the 30 000 substances in Pearson's Handbook on Crystallographic Data for Intermetallic Phases (Villars and Calvert, 1991) are coloured. Wellknown coloured intermetallic compounds are: golden–yellow Cu<sub>5</sub>Sn; blue NiAl; yellow CoAl; yellow CoGa; blue AuGa<sub>2</sub>; blue AuIn<sub>2</sub>; red PdIn; purple AuAl<sub>2</sub>; blue-grey NiSi<sub>2</sub>; and dark blue CoSi<sub>2</sub>.

# Colour formation in intermetallic compounds

The formation of colour in metals is based on metallic bonding between different metals. The strong *metallic bonds* consist of positively charged metal atoms in fixed positions, surrounded by delocalized electrons. Colour results from the electrons in the lower energy levels being excited to higher levels. However, colour in metals can also be formed by intermetallic compounds where strong *covalent bonds* replace the metallic bonds.

Some models have been developed indicating the requirements for obtaining coloured intermetallic compounds. Brief descriptions of these models are provided here, and if more in-depth scientific support to these models/concepts is needed, the reader can consult the referenced papers. The three models are:

- (i) Pettifor's structure maps
- (ii) Hume-Rothery electron concentration
- (iii) Valence electron concentration.

#### Pettifor's structure maps

According to Steinemann (Steinemann, 1990; Steinemann *et al.*, 1997; 2002), coloured intermetallic compounds possess a pseudobandgap, which is an energy range with only a few available quantum states, represented by a valley in the density of states curve. These intense localized bands are found approximately 1.5 to 3 eV below the Fermi level. The following three requirements have been identified by Steinemann in order to obtain coloured intermetallic compounds:

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- (1) The crystal structure of the compound is of high symmetry that has strong features of the band structure, i.e. sharp peaks and valleys in the density of states
- (2) Hybrid *d-sp* bonds for strong covalent hybridization(3) A late transition element or precious metal shifts the Fermi energy appropriately close to the pseudogap.

Steinemann et al. (2002) described how it is possible to establish a relationship between colour and crystal structure in intermetallic compounds by making use of Pettifor's structure maps (Pettifor, 1985; 1986; Pettifor and Podlouchy, 1985). Pettifor's structure maps plot crystal structures of binary compounds  $A_x B_y$  of any stoichiometry to a twodimensional map of some 'coordinates' for elements A and B. Figure 1 shows structure maps for compounds of stoichiometries AB and AB<sub>2</sub>, which could be candidates for coloured intermetallic compounds. The regions marked with dashed lines reveal potential candidates for binary coloured intermetallic compounds. Interestingly, only two crystal structures (Figure 2) dominate these regions, namely bccbased B2 (Pearson symbol cP2) or CsCl-structure for composition AB, and fcc-based C1 (Pearson symbol cF12) or CaF<sub>2</sub>-structure for composition AB<sub>2</sub>. This again confirms the three requirements stipulated above that coloured intermetallic compounds need to have a crystal structure of highest symmetry, ensuring a sufficiently simple electronic structure for distinct absorption bands of high intensity. According to this approach, only the following potential coloured binary gold, palladium, and platinum intermetallic compounds can result:

CsCl structure: PdIn, PdBe, PdMg

CaF<sub>2</sub> structure: PdAl<sub>2</sub>, PtSn<sub>2</sub>, PtGa<sub>2</sub>, PtAl<sub>2</sub>, PtIn<sub>2</sub>, AuGa<sub>2</sub>, AuAl<sub>2</sub>, AuIn<sub>2</sub>.

Element B is of Groups 13 and 14 in the Periodic Table, with the exception of PdMg. Furthermore, PtAl (tetragonal structure) also exhibits colour according to Figure 1 (Steinemann *et al.*, 1997). Interestingly, PtGa and PdGa, which have a B1 structure, but do not exhibit colour, are omitted due to a missing pseudogap. PtMg also does not reveal colour as its B20 structure, although cubic, is of lower symmetry. PtGa<sub>2</sub> andPtIn<sub>2</sub> are stable only at temperatures above 153°C and 674°C, respectively (Steinemann, 1990).



Figure 1—Regions of high-symmetry structure in the AB (a) and AB<sub>2</sub> (b) Pettifor maps. Mendeleev numbers and prototypes (c is cubic, t is tetragonal, o is orthorhombic, h is hexagonal) are shown. Limits for expected coloured intermetallic compounds are shown by the dashed line (Steinemann *et al.*, 1997)

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#### Hume-Rothery electron concentration

An electron-to-atom ratio is stipulated for the Hume-Rothery phases, where the electron concentration (e/a) is defined as the sum of the valence electrons per atom of the compound:  $e/a = 1/100 - \Sigma a_i v_i$ 

where

 $a_i$  is the concentration in at.%

 $v_i$  is the number of valance electrons of element *i*.

The number of valence electrons for platinum and palladium is 0 according to Ekman's rule, and valence electron numbers are 1, 2, and 3 respectively for Groups 1, 2, and 13 (Al, Ga, In) (Steinemann *et al.*, 2002). Table I gives the specific values for the elements and compounds.

Accordingly, the CsCl structure is stable when e/a is approximately 1.1 to 1.7, for example PdIn. Furthermore, the CaF<sub>2</sub> structure is stable if e/a is approximately 2.0 to 2.67 as in the case of PtAl<sub>2</sub>, PtGa<sub>2</sub>, and PtIn<sub>2</sub>.

#### The valence electron concentration

An extension of the Hume-Rothery electron concentration model is the upper limit on the valence electron concentration according to Schlemper and Thomas (1994), which applies to the Zintl phases, for more complex ternary and quaternary compounds. The high number of valance electrons of the precious metals determines the appropriate location of the Fermi level inside the pseudogap, providing absorption bands for creating colour. Eberz (1983) indicated that only intermetallic compounds with valence electron numbers equal to or smaller than about 7 will exhibit colour. Some examples are provided in Table II for various Au, Pd, and Pt compounds (Eberz, 1983).



Figure 2-Crystal structures: (a) CsCl structure, and (b) CaF<sub>2</sub> structure

#### Table I

Number of valence electrons for specific elements and the electron-to-atom ratio of platinum and palladium compounds

Liement, i	· ·
Pd,Pt	0
Al, Ga, In	3
Compound	e/a
Compound	e/a
<b>Compound</b> Pdln	<b>e/a</b> 1.5

#### Table II

Some Au-, Pd- and Pt-based ternary intermetallic compounds of the Zintl-type (derivates of the  $AB_2$  structure). The total number of valenceelectrons,  $N_{val}$  is also indicated (Eberz, 1983)

Colour	Nval			
Gold compounds				
Green-yellow	6			
Green-yellow	6			
Red-violet	7			
Violet	7			
AuLi <sub>0.5</sub> Ga <sub>2</sub> Blue				
Grey	8			
Palladium compounds				
Brown-yellow	5			
Rose	5			
PdLi <sub>2</sub> In Brown-yellow				
ILi <sub>2</sub> Sn Yellow 6				
/IgSn Brown-yellow 6				
Brass-yellow	7			
Violet	7			
Platinum compounds				
Bright-yellow	5			
In Brass-yellow 5				
Sn Yellow 6				
Sn Reddish-brown 6				
Copper-red	7			
Brown-pink	7			
VtMgSb Violet 7				
	Colour Gold compounds Green-yellow Green-yellow Red-violet Violet Blue Grey Palladium compounds Brown-yellow Rose Brown-yellow Yellow Brown-yellow Brass-yellow Brass-yellow Violet Platinum compounds Bright-yellow Brass-yellow Yellow Reddish-brown Copper-red Brown-pink Violet			

Drews et al. (1986) have published interesting results on the optical properties and structures of a number of ternary and quaternary compounds containing platinum or palladium. These compounds are of type Li<sub>x</sub>Mg<sub>y</sub>PS, where P is palladium or platinum and S is tin (Sn) or antimony (Sb). Sometimes *x*=0, in which case one has a ternary compound. The reflection spectra of all these compounds are similar, indicating colours ranging from yellow to purple, e.g. LiMgPdSn (violet); LiMgPtSn (bright red); LiMgPtSb (violet) etc. By varying the relative amounts of Li and Mg in  $Li_{2-x}Mg_xPdSn$  (where x can vary from 0 to 1), Drews *et al.* found that the lattice parameter increased by 1.5% with a colour change from yellow to copper-red and then to redviolet. Figure 3 shows the amount of light reflected as a function of colour (wavelength) for three different intermetallic compounds. The valley in the reflection curve near the green portion of the spectrum leads to stronger reflection at the blue and red ends of the spectrum, resulting in a pink or purple colour. The sharp rise in reflectivity in the blue part of the spectrum is most likely due to increased absorption, resulting from a hybrid resonance between delectrons of a noble metal and conduction electrons.

# Applications

#### Jewellery

The three main colours of caratage gold alloys, namely yellow, red, and white, are well known. The less-known colours of gold include blue, purple, and black. A review of

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coloured gold alloys was published by Cretu and Van der Lingen (1999, 2000). Coloured gold alloys can be produced by three metallurgical routes:

- (i) Alloying with elements such as copper, which results in a more reddish colour; or silver, giving a more white-greenish colour.
- (ii) Coloured oxide layer formation by alloying with an oxidizing element, such as iron, and exposing the alloy to an oxidizing heat treatment.
- (iii) Intermetallic compounds, which are addressed in the present review.

The most popular coloured intermetallic gold compound is purple AuAl<sub>2</sub>, which is formed at a composition of 79 wt%Au and 21 wt%Al. This material can be hallmarked as 18 carat gold, which requires at least 75 wt% gold. Due to the brittleness of intermetallic compounds, jewellers have used the colourful compound as inlays, gemstones, and in bi-metal castings (Figure 4). The melting point of AuAl<sub>2</sub> is 1060°C.



Figure 3—Reflection curves for three intermetallic compounds with the CaF<sub>2</sub> structure (Drews *et al.*, 1986)



Figure 4—Bi-metal castings of micro-alloyed AuGa<sub>2</sub> blue gold (left) and micro-alloyed AuAl<sub>2</sub> purple gold (right) with 95 wt% palladium (Fischer-Buhner *et al.*, 2010)

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Two other intermetallic compounds that are known to produce colours in gold alloys, as also revealed by Pettifor's structure maps, are AuIn<sub>2</sub> and AuGa<sub>2</sub>. The gold-indium intermetallic compound AuIn<sub>2</sub> has a clear blue colour and forms at 46 wt%Au, and AuGa<sub>2</sub> at 58.5 wt%Au has a slight bluish hue. The latter compound can be hallmarked as 14 carat gold. The reflectivity falls in the middle of the visible spectrum and rises again towards the violet end, giving distinctive colours in each case (Vishnubhatla and Jan, 1967). Figure 5 shows the reflectivity as a function of the energy of the incident light for AuAl<sub>2</sub>, AuIn<sub>2</sub>, and AuGa<sub>2</sub> (Saeger and Rodies, 1977).

The inherent brittleness of the coloured gold intermetallic compounds can be improved by micro-alloying additions (<2 wt%), such as additional aluminium, palladium, copper, or silver (Wongpreedee, 2006).

#### Platinum intermetallic compounds

Unlike gold, platinum and palladium have a strong white lustre and act as bleaching agents, making them very difficult to colour by conventional alloying as in the case of gold. Both coloured gold and platinum intermetallic compounds have the CaF<sub>2</sub> structure with alloying elements X = Al, In, and Ga. Klotz (2010) found that interesting colour effects can be achieved by an exchange of gold with platinum while keeping a constant atomic ratio of  $(Au,Pt)X_2$ . For blue gold, increasing platinum content changes the blue AuIn<sub>2</sub> colour towards apricot PtIn<sub>2</sub>.

Mintek in South Africa has found that two distinct colours, namely orange and pink, result by adding different amounts of copper to the PtAl<sub>2</sub> compound (Hurly, 1991; Hurly and Wedepohl, 1993). The optimum compositions for the colours are shown in Table III.

Figure 6 shows the measured CIELab colour co-ordinates (only positive a\* and b\* values) for the three samples in Table III, as well as unalloyed platinum, gold, silver, and some standard gold alloys. The a\* co-ordinate is a measure of the intensity of the red and green colours of the sample: an increasingly positive a\* indicates more red in the sample, and



Figure 5–Reflectivity as a function of the energy of the incident light for the intermetallic compounds: (1) AuAl<sub>2</sub>, (2) AuIn<sub>2</sub>, (3) AuGa<sub>2</sub> (Saeger and Rodies, 1977)

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increasingly negative a\* values indicate more green. Similarly, b\* measures yellow and blue: increasingly positive b\* indicates more yellow, and increasingly negative b\* more blue (ASTM-E308-01, 2001).

Figure 7 shows percentage reflectivity as a function of wavelength for  $PtAl_2$  and other samples containing varying amounts of copper. An increase in the copper content results in a change of colour from the characteristic brass-yellow of  $PtAl_2$  through orange to pink. The sample containing 25% copper has a minimum in the green region of the spectrum (about 500 nm), and the higher reflectivities at the blue and particularly red ends of the spectrum combine to give the characteristic pink colour.

Hurly and Wedepohl (1993) found from X-ray diffraction studies of  $PtAl_2$  with various copper additions that all the samples (up to 25 wt% Cu) had the basic fluorite structure



Composition of three distinct colours for platinum, aluminium and copper compounds

Colour	Platinum, wt%	Aluminium, wt%	Copper, wt%
Yellow	77	23	
Orange	69.3	20.7	10
Pink	61.6	18.4	20



Figure 6—The a\*, b\* co-ordinates of PtAICu samples, as well as those of pure Pt, Au, Cu and some Au alloys (adapted from Cretu and Van der Lingen, 2000 and Hurly and Wedepohl,1993)



Figure 7—Reflectivity curves for  $\mathsf{PtAl}_2$  and  $\mathsf{PtAl}_2$  with Cu (Hurly and Wedepohl, 1993)

 $(CaF_2)$  of PtAl<sub>2</sub>. The lattice parameter increased with copper content as the colour changed. For PtAl<sub>2</sub> with 25wt% copper, the lattice parameter is about 0.8% greater than that of pure PtAl<sub>2</sub>.

As with purple gold, coloured platinum intermetallic compounds lend themselves to be treated like gemstones and can be facetted by using standard gem cutting equipment and techniques. Figure 8 shows a jewellery item with facetted pink-coloured platinum compounds, also known as Platigem<sup>®</sup>.

#### Palladium intermetallic compounds

According to the binary In-Pd phase diagram (Massalski et al., 1986), five In-Pd intermetallic compounds exist, namely In<sub>3</sub>Pd, In<sub>3</sub>Pd<sub>2</sub>, InPd, InPd<sub>2</sub>, and InPd<sub>3</sub>. The In-Pd intermetallic compound with composition 50 at.% (48 wt%) palladium and 50 at.% (52 wt%) indium has a purplish-pink colour. Jan and Vishnubhatla (1967) investigated optical properties and Harris et al. (1968) investigated structures of palladiumindium alloys. Figure 9 shows results of optical measurements for gold and PdIn. More than 95% of incident light is reflected by gold in the infrared and longer wavelength range of visible light. At energies higher than 1.9 eV, the reflectivity falls off rapidly with diminishing wavelength. The yellow colour of gold results from its strong absorption of light above energies of about 2.3 eV. The metal reveals the complementary colour of the absorbed frequencies. With PdIn, the absorption occurs at lower energies, and the colour of the compound then appears as purplish pink, also confirmed by Nomerovannaya et al. (1979). The absorption above about 2.2 eV is associated with a large loss function and interband transitions of hybridized states around the Fermi energy (Cho, 1970). The corresponding CIELab values for PdIn are  $L^* = 70$ ,  $a^* = +12'$ ,  $b^* = +6$ 

Schaffer and Ingersoll (1989) and Steinemann (1990) have investigated the effect of different alloying elements on the PdIn system. A summary of the results is compiled in Table IV.

## Coatings

#### PtAl<sub>2</sub>

Platinum-modified aluminide coatings have been used for several decades as diffusion barrier coatings in aircraft and industrial gas turbines (Pomeroy, 2005). These coatings provide improved resistance to both high-temperature oxidation and hot corrosion. Hot corrosion occurs in gas turbines due to the presence of contaminants such as NaCl,  $Na_2SO_4$ , and  $V_2O_5$  in the gases, which form molten deposits that damage the turbine blades (Rajendran, 2012).

The platinum-modified nickel aluminide coatings can exist in two forms depending on how they were formed. Figure 10 shows the two forms, where (a) indicates the twophase  $PtAl_2 + (Ni-Pt-Al)$ , and (b) a single-phase (Ni-Pt-Al) coating. Platinum is initially deposited onto the nickel-based superalloy by electroplating, then heat-treated under a protective atmosphere. The heat treatment conditions influence the formation of a single- or two-phase microstructure. Subsequent aluminizing results in the platinum-modified NiAl coating. Figure 11 indicates a depth profile of the platinum-modified NiAl coating in Figure 10 (a).



Figure 8—Photograph of Platigems (facetted pink  $PtAl_2+Cu$ ) in a jewellery piece (Mintek)



Figure 9—Reflectivity of gold and intermetallic compound PdIn (Jan and Vishnubhatla, 1967)

Anticipated effect of alloying elements on various properties of Pd-In intermetallic compounds			
Elements	Anticipated effect		
Au (up to 10 wt%)	Increases corrosion resistance, hardness, brittleness		
Mo, Nb, W, Cr (up to 10 wt%)	Decreases thermal expansion and increase strength		
Ta, Ti, Re (up to 6 wt%)	Increases strength and grain refining		
Pt, Rh, Ru, Ir (up to 20 wt%)	Decreases thermal expansion coefficient, increase in corrosion resistance, grain refining		
Zn, Sn, Ga, Ge, Al, Si, B (up to 5 wt%)	Protects alloy from oxidation during melting and reduce the melting point of the alloy		
Sc. Y. La and other rare earths (up to 3 wt%)	Reduces oxidation of allovs – important for bonding with porcelain (dental allovs)		

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Figure 10—Microstructures of Pt-modified aluminide coatings on nickel-based superalloy. (a) Two-phase  $PtAl_2 + (Ni-Pt-Al)$ , and (b) single-phase (Ni-Pt-Al) coating (Pomeroy, 2005)



Figure 11-Depth profile for Ni (♠), Pt (●), and Al (■) for the crosssection shown in Figure 10 (a) (Pomeroy, 2005)

The advantages that platinum offers in barrier diffusion coatings can be summarized as follows (Rajendran, 2012 and references therein). Platinum:

- > Improves the high-temperature oxidation resistance by delaying transformation of  $\beta$ -NiAl into  $\gamma'$ -Ni<sub>3</sub>Al in aluminides. The life of the diffusion coating is depleted when all  $\beta$ -NiAl has transformed into  $\gamma'$ -Ni<sub>3</sub>Al.
- Acts as a catalyst promoting the reaction between aluminium and oxygen.
- Improves the adhesion between the coating and substrate.
- ► Suppresses deleterious spinel formation.
- Retards the diffusion of certain refractory elements to the coating-Al<sub>2</sub>O<sub>3</sub> interface, providing improved isothermal oxidation resistance.

An excellent review by Das (2013) provides information on the importance of the platinum and aluminium contents for the microstructure and oxidation performance of the modified platinum-aluminide bond coatings.

#### AuAl2, AuIn2, and AuGa2

Supansomboon *et al.* (2008) prepared AuAl<sub>2</sub> coatings by vacuum deposition onto heated substrates. The coloured coatings varied in colour from dark silver to light purple, whereas the transmission colours of these coatings varied from light to dark greenish-brown. The colour observed by the human eye was dependent on the texture of the substrate, and the crystallized microstructure and the coating

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thickness affected the transmission colours. The potential use of AuAl<sub>2</sub> as a spectrally selective coating on architectural glass was explored, but the compound was found to be inferior to gold in terms of selective attenuation of the infrared radiation. Furrer *et al.* (2013) found that the light purple colour of AuAl<sub>2</sub> coatings is due to point defects in the film resulting from the deposition method. The intense purple colour can be obtained by heat treating the coating at 350°C.

Supansomboon (2013) produced AuAl<sub>2</sub> and PtAl<sub>2</sub> coatings by a co-sputtering technique, and similar X-ray diffraction patterns were obtained to those of the bulk AuAl<sub>2</sub> and PtAl<sub>2</sub> samples. Figure 12 shows the CIELab colour measurements, in both reflectance and transmittance mode, for AuAl<sub>2</sub> and PtAl<sub>2</sub> coatings of different thicknesses. Potential uses include decorative applications and jewellery.

Studies by Keast *et al.* (2013) indicated that  $PtAl_2$  and  $AuAl_2$  coatings have dielectric functions suitable for sustaining localized plasmon resonances, as verified with EELS and reflectivity measurements. The results suggested that the  $PtAl_2$  compound is a better candidate for the development of strong localized surface plasmon resonances compared to  $AuAl_2$ .

In a project funded by the European Commission on surface engineering of the colour effect for gold alloys, Klotz (2010) found that the electroplating/annealing process was very successful for producing AuIn<sub>2</sub> layers, whereas surface cladding worked well for both AuGa<sub>2</sub> and AuIn<sub>2</sub>, and liquid metal dip-coating for AuGa<sub>2</sub> (Figure 13).

### PdIn

Wang *et al.* (1990) developed a thermally stable, low-resistance PdIn ohmic contact to *n*-GaAs. A layer of



Figure 12—Distribution of chromaticity indices,  $a^*$  and  $b^*$  for coloured intermetallic compound films of different thickness, in reflectance and transmittance modes (a) AuAl<sub>2</sub> and (b) PtAl<sub>2</sub> (Supansomboon *et al.*, 2013)



Figure 13-Gold dip-coated with blue AuGa<sub>2</sub> (Klotz, 2010)

In<sub>0.4</sub>Ga<sub>0.6</sub>As approximately 5 nm in thickness covered the interface between the single-phase intermetallic PdIn layer and the GaAs substrate. Specific contact resistivities and contact resistances of approximately  $1 \times 10^{-6} \Omega$  cm<sup>2</sup> and 0.14  $\Omega$  mm respectively, were obtained.

#### Catalysis, sensors, and capacitors

Mesoporous, also known as nanoporous, gold and platinum can be prepared by de-alloying AuAl<sub>2</sub> and PtAl<sub>2</sub> in a manner analogous to that used in the preparation of Raney nickel catalysts (Van der Lingen *et al.*, 2001). The aluminium is then dissolved from the AuAl<sub>2</sub> precursor by means of NaOH to produce a highly porous gold structure, (Figure 14). Van der Lingen *et al.* (2003) produced heterogeneous catalysts by incorporating transition metal oxide(s) with the porous gold. Furthermore, promoter elements could also be melted with AuAl<sub>2</sub> to improve catalytic activity. These catalysts were tested for CO oxidation activity.

Pattrick *et al.* (2003) studied mesoporous gold catalysts prepared by de-alloying of  $AuAl_2$  for the selective catalytic reduction of NOx by propene under lean-burn conditions for potential autocatalyst applications. It was found that relatively low additions of platinum group metals (1 at.%) caused shifts to lower temperature regions of activity, with the largest shift obtained for rhodium, most likely due to a strong synergistic interaction between rhodium and gold.

Cortie and Van der Lingen (2003) investigated the potential of mesoporous gold for ultra-capacitors, and preliminary work revealed a perceived capacitance of about 15–28 mF as demonstrated for a sample containing 2 g of gold when connected as a cathode. No storage of energy was observed when the gold was connected as the anode. Further work in this field by Mortari *et al.* (2007) on de-alloyed gold indicated that the electrodes showed near-ideal capacitor behaviour under both cyclic voltammetry and potential-step conditions. They proposed that the mesoporous gold electrodes could offer a convenient way to sensitively and accurately amplify the capacitance signal of an electro-chemical sensor.

A significant number of papers have been published recently on nanoporous gold, but the precursor material is 30 wt% gold and 70 wt% silver. A similar de-alloyed structure is obtained for the gold-silver system as for the AuAl<sub>2</sub> system. Potential applications for the nanoporous gold includes: catalysis for oxygen-assisted coupling reactions (Stowers *et al.*, 2013); CO oxidation (Röhe *et al.*, 2013); and electro-

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catalysis/fuel cells (Jin *et al.*, 2013); electrochemical immunoassays and sensors (Sun *et al.*, 2013; Zhu *et al.*, 2013; Li *et al.*, 2013).

Rameshan (2012) studied the formation and thermochemical and catalytic properties of Pd-In near-surface intermetallic phases and correlated the findings to those from the PdZn and PdGa systems. The multilayer PnIn intermetallic phase yielded a highly  $CO_2$ -selective catalyst for methanol steam reforming, although it was not very active in the temperature range 493-623 K. However, in an In-diluted PdIn intermetallic phase, which correlated with the PdZn system,  $CO_2$  formation was largely suppressed and CO formation enhanced via full methanol dehydrogenation.

# Conclusions

Coloured precious metal intermetallic compounds display a range of colours varying from yellow to violet, depending on the specific composition. These coloured compounds have CaF<sub>2</sub> or CsCl crystal structures. The most well-known precious metal intermetallic compounds with CaF<sub>2</sub> structure are purple AuAl<sub>2</sub> and yellow PtAl<sub>2</sub>. Copper additions to PtAl<sub>2</sub> can further result in a colour variation from yellow to orange to pink. In jewellery applications these compounds can be used as gemstones, coatings, or inlays in combination with vellow carat gold or white platinum jewellery alloys. The PdIn compound with CsCl crystal structure has a distinct purplishpink colour, and studies on the effect of different alloying elements on various properties have shown, for example, that additions of up to 20 wt% of other precious metals (Pt, Rh, Ru, Ir) can decrease the thermal expansion coefficient and act as grain refining elements.

Coloured precious metal intermetallic compounds are also used as turbine blade coating material where resistance to high-temperature oxidation and hot corrosion attack is required. The use of coloured precious metal intermetallic compounds as decorative coatings on glass supports is still in the development phase and no commercial products are yet available. De-alloying of precious metal intermetallic compounds can result in mesoporous, also known as nanoporous, materials. These materials have relatively high surface areas, which lend them to further development as catalysts, electro-catalysts, sensors, and capacitors.



Figure 14—HRSEM image of de-alloyed AuAl<sub>2</sub> surface (Van der Lingen et al., 2003)

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Precious metal intermetallic compounds are used in various applications. Although they are inherently brittle, which could restrict their use, this limitation is overcome by using the compounds in powder form, coatings, and inlays with bi-metallic castings.

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