

Metallurgy and processing of coloured gold intermetallics – Part I: Properties and surface processing

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Abstract

Blue and purple gold alloys form in the alloying systems of gold with gallium/indium and aluminium respectively and are known to be very brittle and to possess low corrosion resistance. Taking into account these drawbacks this paper describes the results of a European funded research project. The properties of the blue and purple gold alloys and coatings such as corrosion resistance, metal release rates, hardness and colour and the influence of alloying additions on these properties are presented and discussed. Surface engineering techniques and investment casting were used for manufacturing of jewellery items with selectively coated coloured surface. Coatings of AuGa₂ and AuIn₂ blue gold alloys were applied on 18kt gold and Sterling silver jewellery by electroplating, laser/torch cladding or dipping into liquid gallium. The suitability of blue gold coatings for jewellery purposes will be discussed in the light of reliability and feasibility. The work consists of two parts. Part I describes properties and surface processing techniques while Part II deals with investment casting and related alloy design of coloured gold alloys.

Introduction

Special colours of gold such as purple, blue, brown or black have been attractive in jewellery applications for long time. In principle two ways exist to obtain coloured gold jewellery items, either by surface treatment of karat gold alloys (black, brown or blue gold) or by selection of special alloy compositions possessing the desired colour (purple and blue gold). Reviews about the colours of gold alloys and the different types of alloys were given by Cretu et al. [1], Corti [2] and Bhatia et al. [3]. Different patents on coloured gold alloys and surface treatment techniques for colouring of karat gold alloys exist [4, 5]. Recently, the optical properties of thin purple gold layers were described by Supansomboon et al. [6].

In this work the results of a research project funded by the European Commission on the surface engineering of colour effects for gold alloys are described. In the following, the physical metallurgy of blue and purple gold alloys is discussed, their properties are assessed and methods for jewellery manufacturing are presented. The properties and microstructure of the jewellery items is critically assessed. Potential jewellery applications are described taking into account the properties of blue and purple gold alloys.

Alloy metallurgy

Purple and blue gold alloys form in the alloying systems of gold with aluminium, gallium and indium and are based on intermetallic phases with the stoichiometry AuX₂ (X = Al, Ga, In) [7-9]. The compound AuAl₂ is usually referred to as "purple gold" with nominally 19 karat. AuGa₂ has a bluish-hue and 14 karat while AuIn₂ has a deep blue colour and about 12 karat. The concentration ranges of the intermetallic compounds are very limited. Deviation

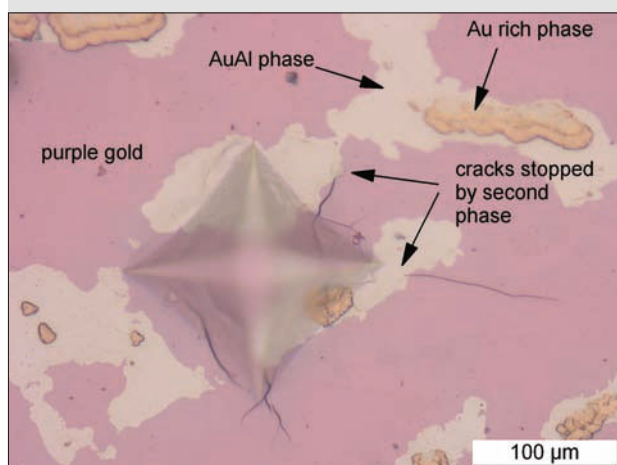
from the stoichiometric composition results in a quick loss of colour. The crystal structure is of the CaF_2 type, hence the intermetallic compounds are very brittle. All intermetallic compounds are congruent melting. Purple gold AuAl_2 has a melting point of 1060°C with deep melting minima for higher and lower gold contents. The blue gold alloys AuGa_2 and AuIn_2 have a low melting point of 491°C and 541°C , respectively. The melting minimum on the gold rich side is much less pronounced compared to the Au-Al system.

Properties of blue and purple gold jewellery

The critical properties of blue and purple gold are brittleness and low corrosion resistance and the influence of alloy composition on these properties was investigated. Further investigations comprised colour, hardness and finishing properties of blue and purple gold.

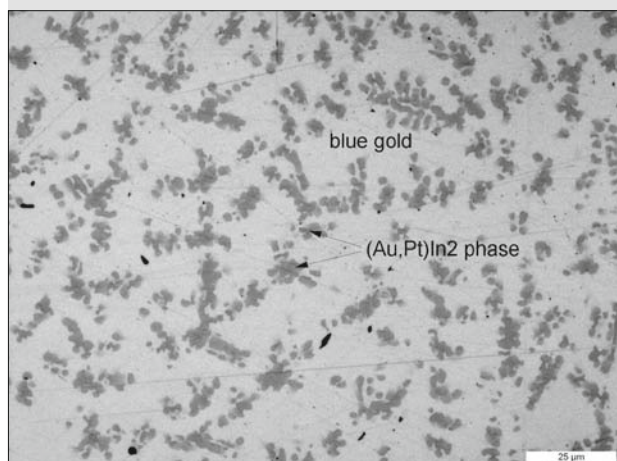
Brittleness of blue and purple gold is an inherent property caused by the low number of slip systems in the intermetallic crystal structure (CaF_2 type). The brittleness of the alloys decreases from AuAl_2 over AuGa_2 to AuIn_2 . A small grained two- or three-phase microstructure is required for the reduction of brittleness and mandatory for allowing use of these alloys for jewellery purposes [4,10]. Therefore, a composition slightly over stoichiometric in gold should be chosen, resulting in a two-phase microstructure of AuX_2 (the coloured gold phase) and AuX (colourless phase) with $X = \text{Al}, \text{Ga}, \text{In}$ (Figure 1). The volume fraction of the second phase should be low in order to avoid bleaching of the colour. The solubility for third alloying element additions such as palladium, copper or silver in purple and blue gold

Figure 1



Three-phase microstructure of alloy $\text{Au}_{76.2}\text{Al}_{19.8}\text{Pd}_4$ (weight %). Crack deflection in the AuAl phase (white) around a hardness indent

Figure 2



Microstructure of blue gold AuIn_2 with addition of 3 weight % PtIr_{10}

Table 1

Composition [mass%]	L	a	b	HV1	Remarks
Au99.9	86	4.7	36.9	28	Fine gold
Au58.5 Ga 41.5	81	-1.0	-2.1	75	Blue gold AuGa_2
Au46 In54	79	-3.7	-4.2	49	Blue gold AuIn_2
Au36 In54 Pt10	81	0.2	-1.3	134	$(\text{Au,Pt})\text{In}_2$
Au26 In54 Pt20	80	2.4	1.3	-	$(\text{Au,Pt})\text{In}_2$
In54 Pt46	78	5.1	12.1	-	PtIn_2
Au79 Al21	67	14.5	-8.9	260	Purple gold AuAl_2
Au79.4 Al 18.6 Pd 2	71	9.1	-1.9	308	
Au76.2 Al 19.8 Pd 4	-	-	-	334	

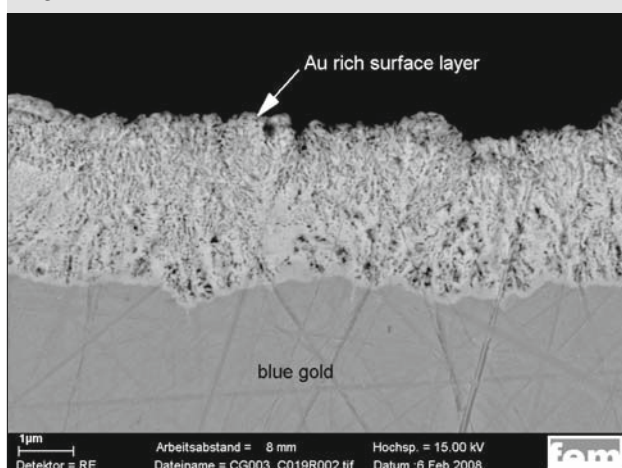
Colour properties (CIE Lab coordinates) and hardness of blue and purple gold alloys in as-cast condition

Table 2

Alloy composition [mass %]	Test method	Au	Al	Pd	Ga	In
Au78.5 Al21.5	(DIN EN ISO 10271)	<0.1	580	-	-	-
Au76.8 Al21.0 Pd2.1	(DIN EN ISO 10271)	<0.1	550	<0.1	-	-
Au76.2 Al19.8 Pd4.0	(DIN EN ISO 10271)	<0.1	395	<0.1	-	-
Au58.5 Ga41.5	(DIN EN ISO 10271)	<0.1	-	-	2444	-
Au46.0 In54.0	(DIN EN ISO 10271)	<0.1	-	-	-	798
Au58.5 Ga41.5	(DIN 1811, 2 days)	<0.1	-	-	683	-
Au58.5 Ga41.5	(DIN 1811, 7 days)	<0.1	-	-	2163	-
Au46.0 In54.0	(DIN 1811, 2 days)	<0.1	-	-	-	382
Au46.0 In54.0	(DIN 1811, 7 days)	<0.1	-	-	-	1226

Metal release [$\mu\text{g}/\text{cm}^2$] in lactic acid (DIN EN ISO 10271) and synthetic sweat (DIN 1811)

Figure 3



Gallium depletion on the surface during corrosion test

is very low. If more than 2 mass % of one of these elements is added the colour of purple gold quickly fades. Interesting colour effects can be achieved by an exchange of gold with platinum while keeping a constant atom ratio of $(\text{Au,Pt})\text{X}_2$. Platinum forms the coloured intermetallic compound with the same stoichiometry PtX_2 ($\text{X}=\text{Al,Ga,In}$) and crystal structure [8]. The effect of platinum on the colour of blue gold AuIn_2 was demonstrated by colour measurements (Table 1). With increasing platinum content the colour changes from blue (AuIn_2) to apricot (PtIn_2). For small additions of platinum the blue colour is slightly enhanced. Furthermore, the precipitation of the PtIn_2 phase results in grain refinement of the blue gold matrix and therefore reduction of its brittleness. In case of AuIn_2 the addition of 3 mass % Pt showed strong grain refinement, which was enhanced by additional 0.3 mass % iridium (Figure 2). The hardness of blue and purple gold

Table 3

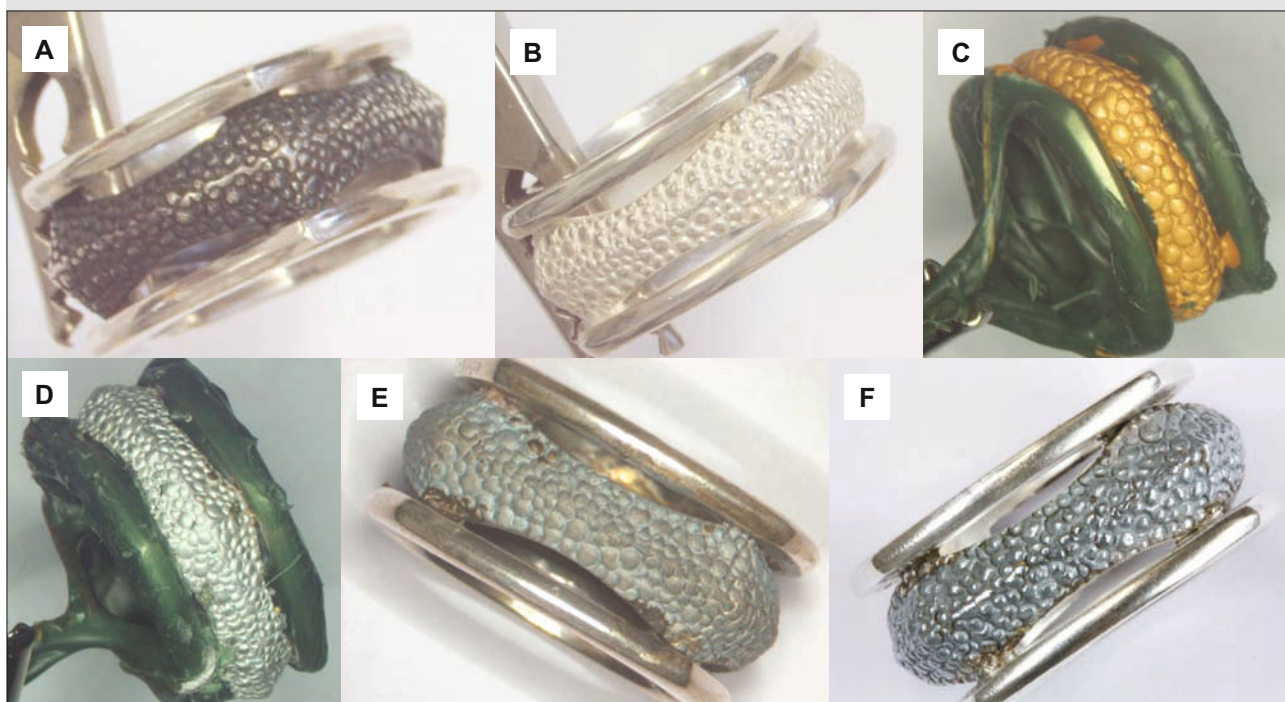
Technique	Suitable for
Electroplating and annealing	Blue gold AuIn_2
Surface cladding	Blue gold AuGa_2 and AuIn_2
Liquid metal dip-coating	Blue gold AuGa_2

Processing techniques for coloured jewellery

alloys differs markedly. While blue gold and its alloys show relatively low hardness below 100HV1 purple gold and its alloys reach hardness values up 334HV1.

Metal release tests were performed for blue and purple gold alloys in artificial sweat (according to DIN 1811) and lactic acid (according to DIN EN ISO 10271). Both tests showed similar results (Table 2). Purple gold alloys showed very high release of aluminium and during the test the colour changed from purple to brownish. With increasing palladium content the aluminium dissolution decreased, but still remains at a high level. The effect of palladium is interpreted as a result of microstructural changes rather than an improvement of the corrosion resistance of purple gold. The blue gold alloys AuGa_2 and AuIn_2 also showed a very high release of Ga and In, respectively. In case of AuGa_2 the metal release was extremely high and within the first hours of the test the colour changed from blue to golden-brownish (Figure 3). The metallographic section revealed a Au-rich, spongy surface layer (2-3 μm thick), which was responsible for the colour change. Blue gold

Figure 4a, b, c, d, e, f



Preparation process for blue gold layers $AuIn_2$ with a Sterling silver ring. a) Original Sterling silver ring, b) Cleaning, c) Masking and gold plating, d) In plating, e) after annealing, f) polished ring

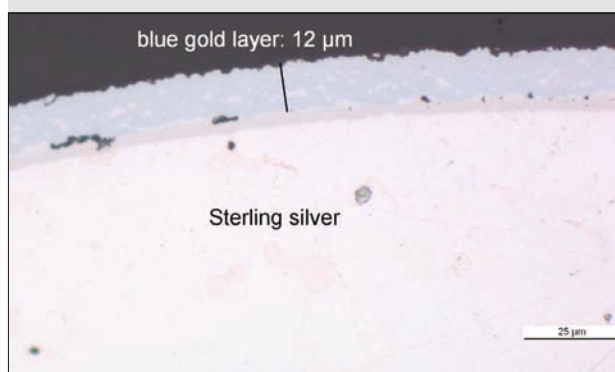
$AuIn_2$ showed no colour or microstructure changes during the test, despite the high metal release. It was not possible to improve corrosion properties of blue and purple gold by alloying with third elements. As a consequence transparent, protective coatings are probably required for jewellery applications.

In terms of brittleness and corrosion resistance $AuIn_2$ appears as most promising candidate for jewellery uses. However, brittleness and low corrosion resistance have to be taken into account in jewellery design.

Some recommendations for jewellery design are listed below:

- Filigree items and parts subjected to external mechanical forces should be avoided
- The jewellery piece should have a frame structure of a ductile alloy holding and protecting the coloured gold item.
- Coloured gold alloys are not suitable to set in stones, because of their brittleness.
- Direct contact with the skin should be avoided, because of corrosion by sweat.
- In a two- or multi-coloured jewellery piece coloured gold alloys might show enhanced corrosion in contact with conventional gold alloys.

Figure 4g

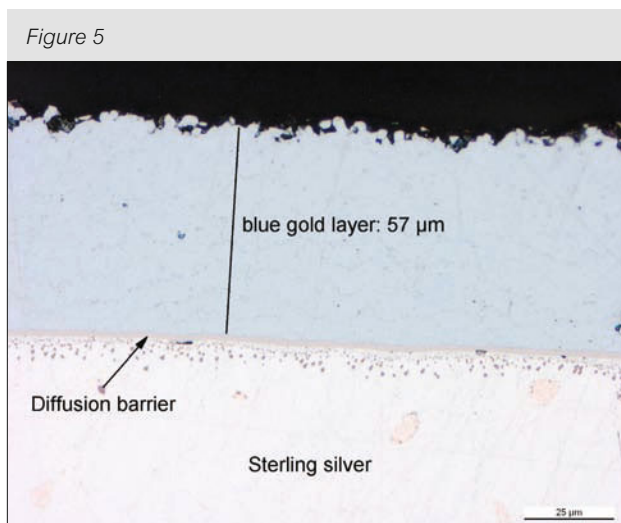


Preparation process for blue gold layers $AuIn_2$ with a Sterling silver ring. g) microstructure

- The protection of blue and purple gold by a transparent, wear resistant coating is probably essential.

Processing techniques

In this chapter different processing techniques for thick coatings of blue gold on karat gold or silver alloys are described. These techniques are based on diffusion surface alloying processes. Not all



Homogeneous and defect-free $AuIn_2$ layer on Sterling silver formed by electroplating and diffusion annealing



a) Wedding bands of 18 karat yellow, white and red gold with $AuIn_2$ blue gold layer. b) Metallographic cross section for red gold

techniques can be applied for the different blue and purple gold alloys (Table 3). As alternative approach, adapted casting technologies are described in part II of this publication.

Electroplating and annealing

Electroplating was used to deposit layers of gold and indium on Sterling silver and karat gold alloys. During subsequent annealing a blue gold layer of $AuIn_2$ was formed. For the gold layer a commercial electrolyte was used. For indium deposition an electrolyte based on Fink-Lester was used [11]. The thickness of the gold and indium layers were adjusted fulfilling the requested atomic percent ratio of Au:In = 1:2. The different steps of the electroplating process are illustrated in Figure 4 for a Sterling silver ring. The gold layer was deposited first to avoid reaction between indium and silver during annealing. Annealing temperature and time to form the $AuIn_2$ layer was based on the reaction-diffusion velocity in the Au-In system [12,13]. During annealing the

gold layer reacted completely with indium to form the $AuIn_2$ layer. Thereby, $AuIn_2$ layers with thickness up to 50 μm could be realized (annealing conditions 160°C/140h, Figure 5). In order to avoid reaction with Sterling silver a diffusion barrier (rhodium or nickel) is required, especially in cases where thick blue gold layers are requested.

The electroplating and diffusion annealing technique was also used for karat gold jewellery. In case of gold substrates indium can be directly deposited on the jewellery item saving costs, efforts and time related to the gold deposition. This was demonstrated for 18 karat white, yellow and red gold wedding bands (Figure 6). A homogeneous and defect-free blue gold layer formed during annealing. The formation of other intermetallic compounds from the gold-indium system was not observed in that case.

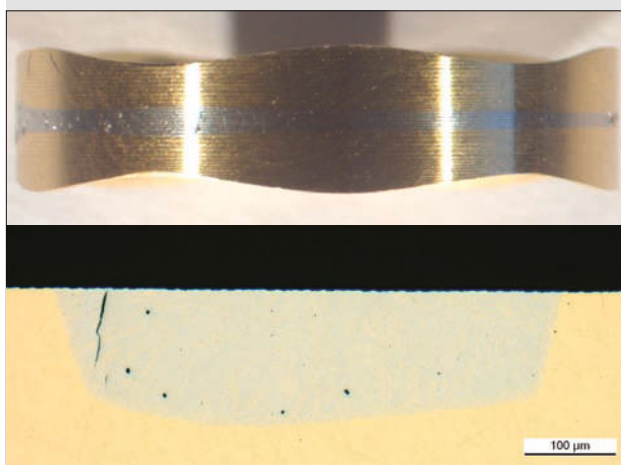
Surface cladding processes

Surface cladding was tested with blue and purple gold rods and powder using a jewellery welding laser or a hydrogen torch. Substrate materials were 18 and 14 karat yellow and red gold and 950Pt alloy. The objective was filling machined grooves on rings with a thick blue gold cladding. The process was hand controlled under protective gas or air in case of using a laser or a hydrogen torch, respectively. The process is difficult to control manually, because of the melting minima observed in the binary systems. Defined, machine controlled process conditions will be necessary in order to achieve constant quality on a high level.

Purple gold can't be alloyed with gold based jewellery alloys by laser / torch welding or adapted casting technologies. Because of the deep melting minimum observed in Au-Al system alloying of purple gold with karat gold alloys results in the formation of low melting phases. However, casting experiments with palladium alloys were successful as described in part II.

Experiments with blue gold were partially successful. A working temperature of about 600°C is sufficient because of the low melting point of blue gold (491°C for $AuGa_2$ and 541°C for $AuIn_2$, respectively). Examples for two jewellery pieces with laser welded blue gold inlays are presented below. On an 18 karat yellow gold ring (Figure 7) complete form filling of a circular groove could be realized. A pronounced colour contrast between yellow and blue gold was maintained. The metallographic cross-section shows a nearly defect-free blue gold inlay with width of

Figure 7



18 karat yellow gold ring with laser welded blue gold inlay and its microstructure

about 0.5mm and a depth of about 140 µm. A two-phase microstructure consisting of the blue gold phase and another more gold rich phase results after laser welding. Similar results were obtained for a 14 karat red gold ring with hydrogen torch welding.

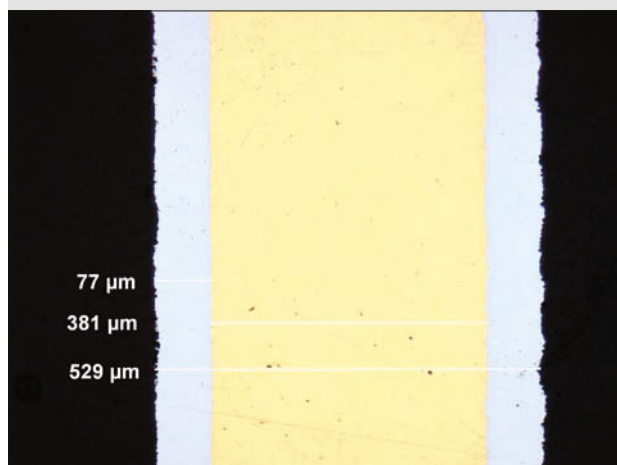
Liquid metal dip-coating

Dipping of jewellery pieces into liquid gallium or indium appeared being a very simple and easy to use technique, especially under workshop conditions. Because of its low melting point of 29.8°C gallium can be melted easily on a hot plate. Dipping experiments were performed at 90°C with fine gold sheets. Once the gallium wetted the fine gold a film of liquid gallium on the gold surface formed, which transformed to $AuGa_2$ at room temperature within a few days. In these experiments defect-free layers of $AuGa_2$ with a thickness of 40-80 µm were obtained for 10-30min dipping time (Figure 8). Unfortunately, such experiments could not be repeated successfully for jewellery items, because of the poor wetting of gold by gallium. In order to avoid oxidation of gallium very clean surfaces and atmosphere would be required. This can only be realized under high vacuum conditions, which are no longer feasible under workshop conditions.

Potential jewellery applications

Conventional jewellery application of purple and blue gold is in form of cast and ground items, which are set similar to gemstones. Due to the inherent brittleness the setting has to provide enough strength keeping mechanical stress away from the blue or purple gold part.

Figure 8



Blue gold layer of $AuGa_2$ on fine gold after dip-coating

In order to manufacture partially coloured jewellery items a selective coating process might be better suited. By such coating the aspect of brittleness becomes much less critical. Based on the experience gathered during the research project electroplating / annealing and an adapted casting technique turned out to be the most reliable processes to obtain coloured layers on karat gold alloys, Sterling silver, palladium or platinum alloys. The electroplating / annealing process works with blue gold $AuIn_2$ by direct electroplating of indium on karat gold alloys. On other materials gold and indium layers have to be deposited with certain thickness ratio. In some cases a diffusion barrier layer might be required.

Poor corrosion resistance is also an inherent property of blue and purple gold alloys, which can't be changed by alloying measures. In metal release tests with synthetic sweat or lactic acid high release rates for aluminium, gallium and indium were found. During the test the colour was lost and blue and purple gold became golden-brownish. This is caused by a gold rich layer, which can be polished off easily to obtain the blue / purple colour again. Blue gold $AuIn_2$ had the lowest release rate, i.e. the highest corrosion resistance and did not show a colour change during the metal release test. As a consequence of the high metal release rates direct contact of blue and purple gold jewellery with skin should be avoided as the released metal might be absorbed by the human body. In bicoloured or multicoloured jewellery where blue / purple gold is in contact with karat gold or other jewellery alloys enhanced corrosion due to local cell formation might occur. A transparent and wear-resistant coating

is probably mandatory to protect the blue / purple gold jewellery from corrosion and to maintain the colour. First experiments with coatings showed promising results and an improvement of corrosion properties.

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