Metallurgy and processing of coloured gold intermetallics – Part II: Investment casting and related alloy design

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Abstract

The attractive color of blue and especially purple gold alloys has always intrigued jewelry designers and producers. The reality of using these colors for jewelry has been very limited, however, mainly due to the inherent brittleness and poor corrosion resistance of this special class of gold alloys. The paper reports on some improvements in crack resistance that are obtained by particular additions to 14k blue- and 18k purple-gold colored alloys. Opportunities to incorporate such colors in jewelry design with these modified, colored-gold alloys using investment casting (as well as the still existing limitations) are discussed. Special attention is given to bi-metal casting technologies that can be used to manufacture multi-colored jewelry. A protective, transparent and wear-resistant coating finally needs to be applied to minimize corrosion and improve long-term stability of the colorful pieces.

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Introduction

The peculiar properties of blue and purple gold colored alloys based on the intermetallic compounds $AuGa_2$, $AuIn_2$ and $AuAl_2$ have been reviewed extensively in former conference proceedings [1] and most recent *Gold Bulletin* articles [2],[3]. The purpose of the present work has been to offer to jewelry manufacturers new or improved opportunities to incorporate these special colored gold alloys in jewelry design by using established manufacturing techniques. Approaching this required work mainly in two directions:

- the development of blue and purple gold colored alloys with improved fracture resistance
- the study and adaptation of processing conditions to produce (multi-) colored jewelry by investment casting, especially bi-metal casting.

Part of this work was carried out in the framework of a European collaborative research project coordinated by FEM (Germany) in cooperation with several industrial partners. Within that project other alternative processing routes than investment casting, namely specialized surface engineering methods, were also studied. The corresponding results are reported in Part I of this work [2]. Both papers have been presented originally at the Santa Fe Symposium on Jewelry Manufacturing in 2009 [16, 17].

Improvement of fracture resistance

It is important to understand the title of this paragraph. Realistically we simply cannot expect an improvement of 'ductility' or 'deformability'. These intermetallic alloys of Au with Al, In or Ga will never behave like alloys that are considered ductile and malleable by jewelers. The reason for this is the special crystal structure in which these alloys crystallize, which is identical to the crystal structure of several ceramics or minerals like fluorite (also known as fluor-spar). It is very unlikely that, despite of substantial in-depth research, it will be possible to obtain blue or purple gold material where ring-sizing, bending, rolling or wire drawing is possible. Instead, a desired property that can be realistically aimed at is that blue or purple gold jewelry can drop to the floor without breaking apart or that castings can be obtained without cracks, from the consumers and manufacturers point of view, respectively.

Intermetallic alloys for specialized industrial applications have been a huge research field for many years [4]. Improvements of fracture resistance and in part even ductility (the latter only for intermetallics with crystal structures different to the fluorite-type structure of blue and purple gold) have been obtained by measures like:

- substantial grain refinement
- macroalloying additions which form ductile phases especially in grain boundary areas
- microalloying additions (<< 1 wt%).

Grain refinement and macroalloying additions (for example of Palladium) have also been suggested and patented for purple gold, as reviewed in [1]-[3], but satisfying improvements probably have not been recognized by jewelry manufacturers. Furthermore, major alloying additions of several wt% also considerably weaken the intensity of the special colors.

In a more recent work, a reduction of brittleness of purple gold reportedly is obtained by a combination of rapid solidification (casting into copper moulds) and alloying with Si and Co (~ 2 wt% total) [5]. The resulting reduction of grain size from usually 50-200 µm down to 2-8 µm leads to ductile fracture behaviour as observed on fracture surfaces. While a quantification of the obtained improvement of fracture resistance is still lacking, it has been stated that the material withstands dropping from the table to the floor. For the same composition, however, less quick cooling like during investment casting will still lead to much coarser grained microstructure and brittle-like fracture surfaces.

The effects of microalloying additions to gold intermetallics like blue and purple gold have not been reported up to date. Microalloying additions lead to some tremendous improvements of mechanical properties of industrial intermetallic alloys, for example Boron in Ni_3Al [6] and Iron or Gallium in NiAl [7]. The mechanisms which can explain the

Figure 1

The 'crashmeter' for testing and quantifying the fracture resistance of blue and purple gold

beneficial effects of microalloying additions have been discussed controversially, but it seems that they act as 'getter' or 'collector' atoms for dissolved impurities like Carbon, Oxygen or Hydrogen (hence so-called interstitial impurities), which otherwise would support the brittle behaviour of these types of alloys [8].

Consequently a screening of different proprietary microalloying additions was carried out at the Legor R&D lab. Eventually promising candidates were identified which substantially improve the fracture resistance of 14k blue gold ($AuGa_2$-based) and also of 18k purple gold ($AuAl_2$-based), the latter so far only in combination with some other macroalloying additions, however. Trials with the $AuIn_2$-based blue gold (composition near to 11k) were not carried out.

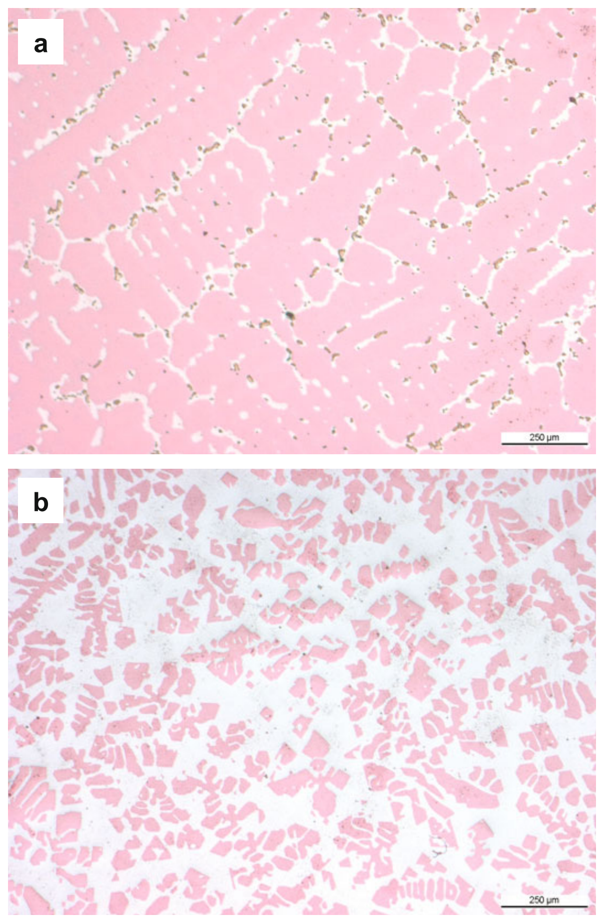
For quantification of the improvement of fracture resistance, a simple and pragmatic test procedure was searched for. Figure 1 shows the 'crashmeter' that was eventually used for testing fracture resistance. The testing procedure was as follows:

- Cylindrical samples of ~10g were dropped through a plastic tube from a height of 0.5 m on the lab floor (Italian paving tile).
- If not cracked, the test was repeated for the same sample from the same drop height up to a total of 5 consecutive tests.
- If still not cracked, the same sample was dropped from a height of 1, 1.5 and 2 m up to five times for

each drop height before continuing from the next higher level, at 2.5 m continuation up to fracture.

- Results were recorded in a simple chart using the symbols 'X' for failure and 'O' for non-failure.

Figure 2



a) Whitish to grayish second phases in purple gold alloyed with Pd (76 Au – 20 Al – 4 Pd); b) Purple crystals embedded in a bluish matrix (58.5 Au – 8 Al – 33.5 In)

The results from the 'crashmeter' tests on 14k blue gold and 18k purple gold are reported in tables 1+2. While a standard 14k blue gold without any third element additions fails already during the 2nd drop from a height of 0.5 m, the microalloyed version survives until a drop height of 2.5 m and eventually fails only after 10 drops from that height. In case of the purple golds no major improvement by microalloying additions alone was obtained so far: Unlike blue gold, microalloyed purple gold samples failed already during the 1st or second drop from 0.5 m. However, in combination with additions of 2 and 4 wt% of Palladium, which itself already provide a quantifiable improvement, the microalloying additions again are very efficient and yield a final resistance until cracking up to a drop height of 1.5 m.

Color variations

An obvious benefit of microalloying additions is that they do not affect the color properties of blue and purple gold alloys. In all cases investigated, no color change was visible and quantifiable for microalloyed samples. As indicated in table 2 and also quantified

Table 1: Results of the 'crashmeter' tests on standard and microalloyed 14k blue gold)

Number of trials carried out on the same piece:
O = specimen passed; **X** = specimen broken

Height of fall (cm)	Standard 14k blue gold alloy ($AuGa_2$)	Microalloyed 14k blue gold alloy
50 cm	**OX**	**OOOOO**
100 cm		**OOOOO**
150 cm		**OOOOO**
200 cm		**OOOOO**
250 cm		**OOOOOOOOOX**

Table 2: Results of the 'crashmeter' tests on standard, Pd-alloyed and microalloyed 18k purple gold

Number of trials carried out on the same piece: **O** = specimen passed; **X** = specimen broken

	deep purple	**purple**		**pale purple**	
Height of fall (cm)	Standard 18k $AuAl_2$	Standard +2wt% Pd	Microalloyed +2wt% Pd	Standard +4wt% Pd	Microalloyed +4wt% Pd
50 cm	**X**	**OX**	**OOOOO**	**OOOOO**	**OOOOO**
100 cm			**OX**	**OX**	**OOOOO**
150 cm					**OOOX**

in [2], the Pd additions shift the colour continuously from a 'deep purple' to a 'pale purple'. A similar effect is also observed for deviations from the exact stochiometry of $AuAl_2$, as well as for other additions to purple gold like Ni or Cu, which like Pd have been suggested to reduce brittleness by formation of a network of ductile second phases in the microstructure. As shown in figure 2a, these second phases are colored grayish or whitish, however, which explains the fading of the intense color [9-11]. Since no such effects are associated with microalloying additions, further research into this topic especially with a focus on purple gold should be promising.

As a side note to color variations it should be reported that, in the framework of the European project, an attempt was made to identify interesting color variations starting from the three gold intermetallic compounds $AuAl_2$, $AuIn_2$ and $AuGa_2$. They all crystallize in the same crystal structure and a former investigation of the corresponding ternary systems revealed some limited mutual miscibility [12]. Hence it was speculated that replacing Al by In or Ga, or vice versa, could probably yield to some colour shifts away from purple or blue toward different hues. However, alloys with compositions lying on the quasibinary sections display two-phase microstructures that are simply composed of purple and bluish phases (figure 2b). As a result $AuAl_2$ is bleached by Ga and In additions, while Al-additions add a purple hue to $AuIn_2$ or $AuGa_2$, which does not really add something new to the already available color spectrum. It is notable, however, that purple hues can also be obtained for 14k alloys.

Conventional investment casting

In order to validate the improvements in fracture resistance, casting trials with the microalloyed 14k blue gold were carried out using conventional investment casting procedures. A standard gypsum bonded investment was used. The liquidus temperature of 14k blue gold ($AuGa_2$) is around 490°C (915°F). The trees shown in figure 3 were successfully cast at 550-630 °C (~1020-1170 °F) with a flask temperature of 350°C (~660°F). The flasks were cooled for 6 min in the flask chamber and left to air cool for up to 90 min before quenching to minimize any mechanical and thermal shocks.

As obvious from figure 3, very good form filling can be obtained with 14k blue gold. A variety of different designs was successfully cast without cracking, which is recognized as a considerable improvement over casting with a standard, non-microalloyed material. But production of too thin and complicated designs, although they could be cast easily, turned out to have little practical sense: They still would tend to crack during finishing when exposed to excessive bending forces, despite of the significant improvements in fracture resistance obtained by microalloying. As a

Figure 3

Trees cast in microalloyed 14k blue gold

Figure 4

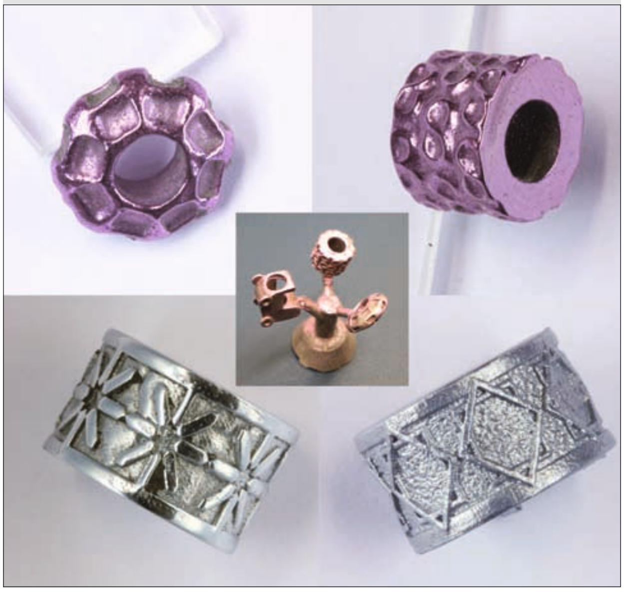
Castings of microalloyed 14k blue gold; a) and b) partial removal of the as-cast oxide layer; c) combination with standard white, yellow and red carat gold. Photo of the butterfly with kind permission of Co. Stephen Webster Ltd., London (UK) general rule tumbling with soft media produces less failures than brushing methods.

18k purple gold has a melting temperature of ~1,060°C (1,940°F). Melting and casting of purple gold is more demanding than the 14k blue gold, since better protection against oxidation is required. Usage of closed systems that allow for evacuation and backfill with protective gas is mandatory. Centrifugal or tilt casting equipment with direct coupling of the induction into the metal is preferred. This allows for quick melting and pouring steps. Otherwise the molten purple gold tends to stick to the crucible walls.

Although crack-free castings can now also be obtained for the 18k purple gold containing palladium and microalloying additions, the resistance against cracking during the finishing process turned out as less good than for the microalloyed 14k blue gold, as expected from the comparison of the 'crashmeter' results. However, isometric shapes (for example bead-like designs) with a wall-thickness of >3 mm were successfully cast and finished.

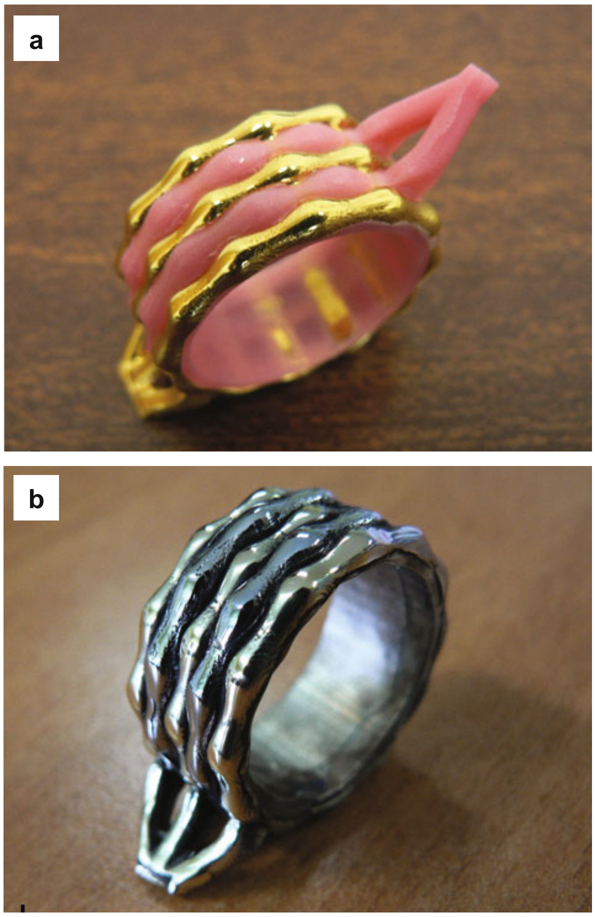
Design considerations
Before pickling 14k blue gold, the as-cast surface is covered by a dark bluish oxide. The oxide can probably be used as a design feature, for example if

Figure 5



Beads cast in 18k purple gold (top row) and $AuIn_2$ - blue gold (~ '11k', bottom row), with kind permission of Co. Reischauer GmbH, Idar Oberstein (D)

Figure 6



Bi-metal casting of a bi-color ring, microalloyed 14k blue + 14k green-yellow gold

it is only partially removed from a rough or structured surface as indicated in figures 4a and 4b.

Another aspect is the enhancement of the blue color by combining it with the conventional carat gold colors as shown in figure 4c. A further benefit of the configurations shown in figure 4c is the protection of the blue gold items by embedding them in a 'normal' ductile matrix.

The safest solution for castings in blue or purple gold is provided by isometric shapes with cross sections of probably > 3mm. For items like the 'beads' shown in figure 5 there is a minimum danger for excessive bending forces during either finishing or wear by the consumer. These items were cast by Company Reischauer GmbH, Idar Oberstein (D), using a table-top vacuum tilt casting machine Indutherm MC15, which is especially suitable for small scale production or casting of prototypes. Usage of vacuum is beneficial for blue gold but mandatory for purple gold casting due to the strong oxidation properties of the Aluminum contained in the purple gold.

Bi-metal investment casting
Bi-metal casting is a specialized casting technique that is only scarcely used in jewelry production despite of its great potential and profound published practical advice for successful application [13].

On the basis of the former experience with blue and purple gold investment casting it has been supposed that bi-metal casting combines several benefits for production of multi-colored jewelry involving the specially colored alloys:

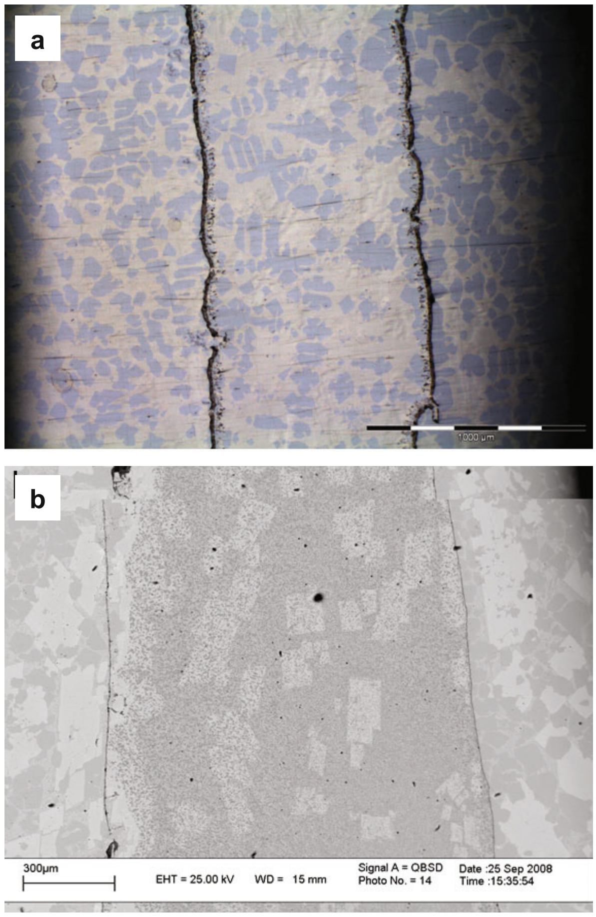
- The blue or purple gold colors can be enhanced by the color of a second alloy.
- The blue or purple colored parts or areas can be mechanically protected by a 'framework' of a stable and ductile second alloy.

Bi-metal casting is a 2-step casting process. In the first step, the first part of the pattern is made in the higher melting alloy by conventional investment casting (alternatively also any other technique). The remaining part of the pattern then is injected in wax on top or around the first part as indicated in figure 6a. After regular investing, dewaxing and burnout, the second part is cast in the lower melting alloy, figure 6b.

As explained in much more detail in [13] not every alloy combination can work: A minimum difference of 100°C between the melting ranges of the two alloys is suggested. Furthermore a proper selection of casting parameters and process control is required to obtain a good bond between the different metals. High-melting and non-oxidizing alloys like 950 Pt and 950 Pd were identified as particular suitable for preparation of the first part of a pattern in combination with all types of carat gold alloys for the 2nd part of the pattern. Also the mass ratio between the two parts was identified as important parameter.

Bi-metal casting of 14k blue gold with 14k yellow-green or 14k white gold
14k blue gold is melting at a very low temperature of ~490°C (915°F). Hence it was supposed that bi-metal casting should work well and easy in combination with other 14k alloys which melt at much higher temperature.

Figure 7



Metallographic cross sectional analysis of bimetal castings. a) Optical microscopy and b) Scanning Electron Microscopy – pictures of bi-metal castings of microalloyed 14k blue combined with a) 14k green-yellow gold and b) 14k Pd white gold

Figure 8

950 Pd casting with injected wax for the 2nd bi-metal casting process step; with kind permission of Vendorafa-Lombardi Srl, Valenza (Italy)

In the European collaborative project, bi-metal casting trials were carried out and analyzed by Legor with a focus first on 14k blue gold in combination with a 14k green-yellow gold with a melting range of 810-845°C (1490-1555°F). The rubber moulds for the 2-step process were provided by the Jewellery Industry Innovation Centre at the Birmingham City University (UK). A partially finished bi-color ring is shown in figure 6b. It cannot be clearly seen from this picture, but the colors did not come out as expected for the complete pieces. Despite of the comparably large difference between the liquidus temperatures of the two alloys and the low flask temperature of 350°C (660°F) partial mixing of the two alloys occurred during the 2nd casting step. This was also confirmed by the metallographic analysis shown in figure 7a. In large areas a non-homogeneous microstructure develops with blue gold phases embedded in a green-yellow gold matrix and vice versa. Furthermore a thick oxide layer at the interface between the two parts is revealed, which formed during the burnout process on the surface of the yellow-green colored part. Such a thick interface oxide layer needs to be avoided since it can weaken the bond between the two parts [13].

In a second set of bi-metal casting trials, a much higher melting 14k Pd-based white gold with a melting range of 1000-1090°C (1830-1995°F) was combined with 14k blue gold. The white gold parts were coated with a galvanic Rh layer before injecting the wax for the 2nd bi-metal casting process step. The metallographic analysis shows much less oxidation at the interface between the parts, figure 7b. Better results in terms of color stability and separation were also obtained on finished surfaces. But even for this alloy combination, with a temperature difference larger than 500°C (T > 900°F) between the liquidus temperature of the blue gold and the solidus temperature of the white gold, the outcome depends strongly on the (local) mass ratio between the white and blue gold parts. Figure 7b shows that a non-homogenous microstructure can develop again in an area with interpenetrating parts of a wall thickness of ~ 1 mm. Detailed analysis revealed Ga-rich phases embedded in a Pd-rich matrix and vice versa.

The possible metallurgical reasons for this behavior are: Ga is a very low-melting element and diffusion into the solid metal of the 1st part leads to a sudden decrease of its melting range so that it can partially melt and mix with the blue gold. In addition it can be speculated that $AuGa_2$, as most intermetallic alloys, has a high heat of formation which is released during solidification and therewith slows down the cooling process and extends the time for diffusion and mixing of compositions.

Figure 9

Bi-metal castings of microalloyed 14k blue gold (left) and microalloyed 18k purple gold (right) with 950 Pd; with kind permission of Vendorafa-Lombardi Srl, Valenza (Italy)

As a consequence of all our studies, which involved different designs, multicolored jewelry that combines 14k blue gold with yellow, red or white gold can be successfully manufactured via bi-metal casting but as a general rule small amounts of blue gold should be used in the design in relation to the yellow, red or white colored part.

Bi-metal casting of 14k blue gold or 18k purple gold with 950Pd

The bi-metal casting approach was further developed in cooperation with Co. Vendorafa-Lombardi Srl, Valenza (Italy). Taking into account the former results and responding to the desire to use also 18k purple gold, which has a melting point of 1060°C (1940°F), it was decided to use 950Pd for the 1st and main part of the design. Starting from existing design concepts of Lombardi, rubber moulds for the 2-step process were once more prepared by colleagues from the JIIC at BCU (UK). Wax injected items for the 2nd process step are shown in figure 8. Castings were carried out using the microalloyed versions of 14k blue and 18k purple gold (the latter with 4 wt% Pd) at flask temperatures of 300-350°C (570-

660°F) and 600-650°C (1100-1200°F), respectively. Attractive color contrasts with the 950Pd and well color separation were obtained successfully in both cases for different designs as shown in figure 9.

Brooches and rings comparable to the ones shown in figure 9 have been worn constantly by test persons so far without failures or cracking, which confirms that good bonding and stability was achieved by a combination of proper design, bi-metal casting process parameters and improved alloy properties. The colors remained practically unchanged, with a tendency to slight discoloration (browning) for the purple gold. Although the discoloration can be easily removed for example by buffing, somehow comparable to removing tarnish layers from sterling silver, there is probably a need for application of protective surface coatings.

Protective coating against corrosion and discoloration

Blue and purple gold alloys have been reported already to have poor corrosion resistance and a tendency to discoloration [2], [14] and [15]. High metal release rates and discoloration were observed in standardized lab tests where test pattern were immersed for prolonged time at human body temperature in standardized media like artificial sweat, artificial saliva or a sulphuric solution. Although the lab testing conditions need to be considered as more severe than real-life conditions, and field-tests like the ones indicated in the former paragraph have yielded much less alarming results than it could have been expected from the lab tests, it is reasonable to recommend the application of protective coatings to minimize corrosion and increase the lifetime and long-term color stability of the colorful pieces.

The requirements for suitable protective coatings are:

- High protection against tarnishing and corrosion in all environmental conditions relevant for jewelry.
- Easy-to-apply, cheap.
- Transparent without any color change with time.
- High wear resistance.

State-of-the-art passivation treatments are cheap and are known to protect sterling silver from tarnishing during shipping and long storage periods. However, their wear resistance is low and a long-term protection cannot be expected. Thin transparent oxide layers can be deposited on surfaces by techniques like Physical Vapour Deposition, but the technology and equipment required is expensive.

A viable alternative is provided by transparent lacquers. An extremely wide number of lacquers is available on the market. The main differentiation is between water-based and solvent-based lacquers. Although a water-basis would be considered less harmful than solvent-based lacquers, their surface properties and wearing resistance are known to be less promising. Among the solvent-based lacquers, transparency may vary significantly. The most wearing resistant, solvent-based lacquers are the two-component lacquers. At the end of their application, they need to be heat treated at 60-80° for ~ 1 hour in order to enhance their wearing resistance. The benefit of lacquers is their easy application by dipping or spraying. Recently, a new bi-component lacquer has been developed by the Legor R&D lab for costume jewelry (low carat gold, brasses, bronzes and also sterling silver) which exhibits excellent long-term protection against tarnishing and corrosion. In our trials its wear resistance proved to be superior to other lacquers and even to galvanic rhodium plating treatments.

Consequently, metal release tests in artificial sweat were carried out in our lab on 14k blue gold ($AuGa_2$-based), which has the highest metal release rate from the three colored intermetallics according to [2]. In our tests the metal release rate of the microalloyed 14k blue gold for the lacquer-coated samples decreased to 10% of the value obtained for non-coated samples. A discoloration was observed for the non-coated samples, but was absent for the coated samples. It is therefore concluded that transparent and wear-resistant 2-component lacquer coatings are available, that fulfill the requirements listed before and which can be recommended to protect blue and purple colored, as well as multi-colored jewelry produced by for example bi-metal casting, against tarnishing, corrosion and discoloration.

Conclusions

New opportunities for blue and purple gold in jewelry are provided by the following developments:

- Micro-alloying substantially increases the fracture resistance of 14k blue gold as well of 18k purple gold (the latter in combination with further 3rd element additions like Pd) without affecting the color.
- Crack-free castings of manifold design can be obtained with micro-alloyed material using conventional investment casting techniques.
- Bi-metal casting techniques are particularly

suitable for manufacturing multi-colored jewelry which combines blue or purple with white color (provided by high melting white alloys like Pd950).
- Protective, transparent and wear-resistant coatings based on hardenable 2-component lacquers are recommended to minimize corrosion and improve long-term color stability of jewelry containing blue or purple parts.

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