New deeply coloured 18-K gold materials built by nanotechnologies

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Abstract A new way to elaborate coloured carat gold materials has been developed. Instead of using traditional metallurgy route, we built a new 18-K bulk material using nanostructured gold particles. The resulting colour is the consequence of a well-known property of gold nanoparticles: the surface plasmon resonance effect. Depending on the chemical environment around the nanoparticles, their shape and size, it is possible to tune the colour of gold. Thanks to this property, it is possible to obtain a large panel of colours not achievable via conventional alloying route. Here, we focus on one hybrid nanostructured material: Au-SiO₂. The development of a new synthesis route enables us to obtain nanostructured micrometric powders that can then be pressed to obtain a bulk material. The resulting nanocomposites are characterized by means of energy-dispersive X-ray spectroscopy (EDX), fire assay, TEM and spectrophotocolorimetry. All these characterizations have shown that our composites exhibit a gold content superior to 75 % by weight and have a much more vivid colour than classical coloured gold. The new composites are therefore deeply coloured 18-K materials.

Keywords Coloured gold · 18-K gold · Gold nanocomposite · Gold nanoparticles · Surface plasmon resonance

Introduction

Since the earliest time, due to humanity's attractiveness for gold, this noble metal had received a lot of attentions in

particular from alchemists and metallurgists. Alchemists were looking for potable gold [1] and transmutation [2–4]; metallurgists were looking into new kind of gold alloy. One of the most important phase diagrams is the well-known Au-Ag-Cu ternary system [5]. This metallurgical system consists in an eutectic system (Ag-Cu) and two binary complete solid solutions (Au-Ag and Au-Cu). Thus, at any temperature, as long as the metal is solid, the ternary system displays either a single-phase ternary solid solution or a biphasic region [6] (Au-Cu diagram displays organized phases as shown in [6]). The yellow, red and green colours achievable with this system are obtained by varying the ratio of Au, Ag or Cu, as shown on the gold triangle (Fig. 1) [7, 8]. More colour variations can be obtained by the addition of nickel (Ni), zinc (Zn), palladium (Pd), cadmium (Cd) or manganese (Mn). However the incorporation of nickel, cadmium and manganese is not desirable. Nickel and manganese are allergens; cadmium oxide (CdO) is very toxic and irritant to the respiratory system, causes damages to the kidney and is carcinogen [9]. Thus, if the alloy has to be at least 12 K, the attainable colour range is restricted.

The colour of typical metals is described as such: high luminance, very desaturated and dominant wavelengths are of a very limited range. A colour can be reproduced by mixing white light with spectrally pure light. Different proportions give a range of saturation, from white (0 % of the spectrally pure light) to the spectrally pure shade (100 % spectrally pure light) which is the most intense colour available of that hue. Saturation refers to the position on the scale. The dominant wavelength describes the hue. Luminance is a technical term which correlates well with brightness [6].

It is possible to obtain gold with higher levels of saturation with intermetallic compounds [9–12]. The most famous one is the purple gold, which is formed of 79 wt.% Au and 21 wt.% Al: AuAl₂ [13]. The gold content being above 75 wt.%, it is considered as an 18-K alloy. Blue gold can be obtained with the following two intermetallic compounds: AuGa₂ and

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Fig. 1 The gold triangle. Relationship between composition and colour in the Au-Ag-Cu ternary alloy system showing the limited range of colour achievable via classical alloying

AuIn_2 . None of them can be considered as 18-K gold alloys since their gold content is respectively 58.5 and 46 wt.%. In any case, those alloys are very difficult to work with in traditional jewellery

or watchmaking techniques since they are very brittle. As a consequence, they are often faceted and used as gemstones or inlays. Table 1 summarizes the different coloured gold obtained by alloys and/or intermetallic compounds.

A third method to obtain coloured gold alloys is through the surface oxide layers [9, 10]. After a heat treatment in air, some atoms of the alloyed metals can move to the surface and form oxides. This can lead to deep colours such as blues, browns, blacks and greens. Elements used in the alloys can be one of the following: cobalt (Co), nickel (Ni), iron (Fe), ruthenium (Ru), chromium (Cr) and so on. However, the oxide layers formed with this technique are usually very thin, leaving the pieces vulnerable to surface damage such as scratches or pitting. To our knowledge, those were the only ways to get coloured precious gold pieces with metallurgical methods.

Using the nanotechnology approach, a completely new range of deeply coloured gold can be obtained. In the past, large pieces of materials coloured by gold nanoparticles have been realized; one can cite the famous Lycurgus Cup (400 AD) [14–16] or the stained glass of the Cathédrale Notre Dame de Paris [17–19] (France). These pieces were realized by master glassmakers using gold salts. The colouration of the glass comes from the in situ reduction of these salts, leading to nanoparticles. However, the glassmakers did not know that they were using nanoparticles to colour their makings. It is

Table 1 Composition and colour of traditional gold alloys obtained through standard metallurgical methods

Name of the alloy	Au		Alloyed Elements					
	% weight	Caratage	Nature	% weight	Nature	% weight	Nature	% weight
0N	58.50	12	Ag	30–34	Cu	7.50–11.50		
1N	58.50	12	Ag	24–26.50	Cu	15–17.50		
2N	75	12	Ag	15–16	Cu	9–10		
3N	75	18	Ag	12–13	Cu	12–13		
4N	75	18	Ag	8.50–9.50	Cu	15.50–16.50		
5N	75	18	Ag	4.50–5.50	Cu	19.50–20.50		
6N	75	18	Cu	25				
Yellow gold	80	19.20	Ag	10	Cu	10		
Green gold	80	19.20	Ag	20				
Red gold	80	19.20	Cu	20				
White gold	80	19.20	Cu	10	Ni	5	Zn	5
Red gold	91.6	22	Cu	8.4				
Yellow gold	91.6	22	Ag	5.5	Cu	2.9		
Grey gold	75	18	Ag	15	Cu	10		
Red gold	75	18	Ag	10	Cu	15		
Green gold	75	18	Ag	25				
Purple gold (AuAl_2)	79	>18	Al	21				
Blue gold	46.00	<12	In	54				
	58.50	<18	Ga	41.50				
White gold (rhodiumized)	75	18	Pd	15	Ag	10		
	75	18	Pd	25				

only a few hundred years later, thanks to new analysis methods, that it has been discovered that the gold nanoparticles were giving the colour to the glass. The aforementioned pieces of fine art cannot however be qualified as precious from a jewellery point of view as they contain a low amount of gold.

The special colouration of these pieces is obtained through the surface plasmon resonance (SPR) effect. When metal nanoparticles are submitted to an electromagnetic field, they polarize. This leads to the collective oscillation of electrons at the surface of the nanoparticles. A specific frequency of the electromagnetic field is absorbed by the plasmon oscillations: this frequency is named the surface plasmon resonance. Thus, macroscopically, nanoparticles present an opposite colour to the absorbed frequency. The SPR depends on several parameters, such as the nature of the metal, the shape [19, 20] and the polarizability [21, 22] of the particle, its surface as well as its environment [20, 23, 24].

The surface plasmon resonance of gold nanoparticles has been extensively studied in the last few decades. Turkevich has presented a robust method to synthesize gold nanospheres [25], the resulting solution usually presents a single SPR around 520–530 nm. Since then, numerous methods based on Turkevich's one have been developed [26–29]. They mostly provide well-defined spherical gold nanoparticles. However, spheres are not the only shape that can be synthesized. Depending on the experimental conditions, cubes [30], decahedrons [30], octahedrons and rods [20, 31, 32] can also be obtained. Each shape and size [20] synthesized presents specific absorption spectra. Thus, depending on all these parameters, colours like blue, purple, pink, red or even green are obtainable [33].

This specific colour property has given rise to the use of gold nanoparticle as a pigment for various applications from the coloration of wool [34] to the coloration of paint [35].

Several attempts of using gold nanoparticles in the jewellery industry have been done. One can cite the use of gold nanoparticles as a pigment for ceramics with a content up to 5 % in mass [36]. However, with this attempt, they were not able to produce a material containing 75 % in mass of gold.

In this paper, we report a new method to obtain deeply coloured gold powders thanks to the SPR effect of gold nanoparticles. The innovation here is that we work with silica-coated gold nanoparticles instead of classic bulk gold alloyed with different elements. Indeed, the addition of a dielectric shell (silica) around the gold nanoparticles modifies the SPR effect, allowing us to obtain different colours. The gold content can be fine-tuned from 50 to 90 wt.% by controlling the thickness of the dielectric shell. The approach developed here is a two-step method: the gold nanoparticles are first produced and then coated. After precipitation, the particles are filtered, dried, annealed and then can be pressed into pellets so as to obtain a bulk material.

Experimental section

Characterization material

The annealed powders are characterized using a Philips CM20, 200 kV equipped with a LaB₆ filament transmission electron microscope. The powder is directly put on the TEM grid without the use of a solvent.

The obtained pellets are imaged using a JEOL JCM-6000 equipped with energy-dispersive X-ray spectrometry (EDX) operating at 15 kV; the EDX analysis is performed on the same apparatus.

The colour determination was carried out on a spectrophotometer, Konica Minolta CR-5, D65 light source, 10° observation. The spectral curve is obtained on a Konica Minolta CM-5 spectrophotometer, D65 light source, 10° observation, specular included.

Fire assay test was carried out by Bureau Central du Contrôle des Métaux Précieux of Switzerland (Berne, Switzerland).

Chemicals

The ultrapure water comes from a MQ-8 apparatus and has a resistivity of 18.2 M Ω cm⁻¹ (ultrapure water), Merck Millipore. Hydrogen tetrachloroaurate (III) (HAuCl₄·3H₂O, 99.99 %) is purchased from Sigma Aldrich. Tetraorthosilicate (TEOS), *N,N*-dimethylformamide (ReagentPlus, ≥99 %) and tri-sodium citrate (ACS reagent, ≥99 %) were purchased from Sigma Aldrich. Isopropyl alcohol is obtained from Carlo Erba. Ammonium hydroxide solution (28 % NH₃) is purchased from Alfa Aesar. All the reagents are used as received, without any further purification.

Au stock solution

A stock solution of 250 g. L⁻¹ gold (III) chloride hydrate is made with ultrapure water.

Synthesis of nanoparticles

The synthesis A1 is a two-step process derived from the Turkevich's method [25–27]: the nanoparticles are synthesized before they are coated with silica. It is performed in a 60 L glass line reactor. The reactor is filled with 16.3 L of ultrapure water and 11.78 mL of the gold stock solution. The solution is thoroughly mixed and heated to the reflux point, around 130 °C. Then, 0.686 L of a 2 % tri-sodium citrate solution is added. The solution discolours and quickly turns red. The heating is maintained for a short period of time and then the solution is let to cool down. On cooling, 32.5 L of isopropyl alcohol is added to the reactor and then 13 mL of TEOS is added followed by 0.3 L of ammonium hydroxide solution. The solution quickly turns dark

blue. After a certain time of mixing, small dark-coloured flakes are forming in the solution. The reaction is then stopped and the solution is filtered. The precipitate is washed with ultrapure water. The dark-coloured cake is removed from the apparatus and put in a drying oven.

The entire powder obtained is then annealed under air in a muffle furnace (800 °C for 2 h). A coloured powder is obtained. Using the above synthesis and post thermal treatment, 1.6 g of coloured material is obtained.

Fabrication of pellets and sintering

To obtain a pellet, two batches of synthesis are mixed since about 3 g of material are sintered. The coloured powder is inserted in a 10-mm metallic die. The die is then placed under a uniaxial force of 60 MPa for 10 min. The obtained pellet is removed from the die and pre-sintered for 5 min in a muffle furnace previously set at 850 °C. A compact piece of material is obtained.

Fig. 2 EDX analysis coupled with a MEB observation of the synthesized powder

Fig. 3 Transmission electron micrograph of gold nanoparticles in a silica matrix

Results and discussion

Powder

To determine the composition of the synthesized powder, the samples are analysed by means of energy-dispersive X-ray spectrometry. The EDX analysis is presented in Fig. 2 as well as the SEM image of the acquired area. By tailoring the amount of silica precursor at a constant gold amount, it is possible to adjust the composition of the powder. Indeed, the less silica precursor (TEOS) is added, the higher the gold content will be, and reciprocally. Nevertheless, there is a minimum amount of ceramic precursor to add to the reaction as its role is to prevent the agglomeration of gold by coalescence or/and Ostwald ripening mechanisms. All the analysis results are gathered in Table 1.

Figure 3 shows typical images of the gold nanoparticles with their shell. They have been taken on the edge of the aggregate so that the electron beam could go through all the materials. The gold nanoparticles have a mean size of 50 nm and are surrounded by silica. This synthesis is a variation of the Turkevich method [25–27], one of the most studied and used method to produce gold nanoparticles. It means that the control of the nanoparticles size has been studied for a long time and therefore is easy to reach. It is worth noting that the gold nanoparticles are not individually coated with silica as expected for a regular core shell structure. This is a key advantage for us as the agglomerate microparticles can be easily filtered in our system. If the gold particles were individually coated, we would have to use centrifugation to

collect them, which is much slower and not financially viable for industrial applications. It can also be noticed that in a ceramic flake, each gold nanoparticle is separated from another.

Using the same synthesis method but varying the amount of silica precursors and gold salt, different coloured gold powders were obtained (syntheses A2, A3 and A4 (Tables 1 and 2)). The colour of the powders is then measured with a spectrophotometer; this data is gathered in Table 1. This table shows three variations of the synthesis in which the silica precursor ratio has been tuned. This results in otherwise-coloured gold powders with a gold content varying between 12 and 18 K. The comparison between these values and the ones presented in Fig. 4 shows a clear difference in terms of colour.

The annealing induces the densification of the ceramic surrounding the gold nanoparticles; this prevents the agglomeration by coalescence and/or Ostwald ripening mechanisms. Unless the ceramic coating is altered, there is no reason that this powder should evolve towards the formation of metallic gold chunks. Nevertheless, the heating temperature should not be excessive for a long period of time. The powder annealed at 1200 °C for 2 h totally decolours due to the agglomeration of gold nanoparticles. Indeed, the gold and the silica present in the powder have completely demixed which results in gold pearls with silica particles.

Pellet

The silica-coated gold is then compacted and sintered. This is a key stage in our process. If the powder is pressed with a too important force, the silica flake can be damaged: the colour can be impaired and it can lead to the formation of classic yellow gold. Concerning the sintering, the conditions have to be optimized; this will be the subject of a further study.

The resulting pellet is then characterized in terms of gold content and colour. The gold composition is measured with two different methods. The first one uses a SEM equipped with EDX. This analysis is performed on a small chunk of the pellet. The measured gold content is 80.1 wt.%. The obtained image and spectrum are compiled in Fig. 2. The second method used is the fire assay technique. Using this technique, a gold content above 87.8 % was determined. A difference of gold rate can be noticed between the two method used. The

Table 2 Composition and colour of gold-based nanocomposite obtained via the new nanotechnology methods

Name of the alloy	Au		Nanocomposite composition		Colour coordinates	
	% weight	Caratage	Nature	% weight	a*	b*
Synthesis A1	80.10	19.2	SiO ₂	19.90	18.31	21.82
Synthesis A2	52.00	~12	SiO ₂	48.00	22.05	30.20
Synthesis A3	85.00	20.4	SiO ₂	15.00	16.77	30.20
Synthesis A4	70.00	16.8	SiO ₂	30.00	20.24	17.76

Fig. 4 Colour coordinates of Varinor standard gold alloys and of the presented material in the a^*b^* space (2N, 3N, 4N, 5N, 6N, 22-K yellow gold, 22-K red gold and A1-derived material)

EDX provides a lower gold content, which can be explained by the surface state of the analysed piece. Nevertheless this technique is very useful to determine the range of the content

in the sample. The EDX spectrum presented in Fig. 3 shows that our sample is only composed of Si, O and Au. The low amount of carbon detected on the spectra can be due to a

Fig. 5 Spectral curves of the 18-K deep red gold and the standard gold alloys provided by Varinor (2N, 3N, 4N, 5N, 6N, 22-K yellow gold, 22-K red gold and A1-derived material)

Fig. 6 Pellet of the presented material

surface contamination or to the carbon tape used to fix the sample during the SEM observation. As the cupellation technique is a standard method in Switzerland, we will preferentially take this result into account. However, both techniques show the formation of 18-K red-coloured gold.

The colour of the piece is measured with a spectrophotometer, same specifications as cited beforehand. The a^*b^* values are respectively 18.31 and 21.82. Figure 4 presents a plot of our measurement in the a^*b^* space. It is compared to the values of the 2N, 3N, 4N, 5N, 6N, 22-K yellow gold and 22-K red gold standards provided by Varinor. With the a^*b^* system, the higher the a^* value is, the redder it is. Even though the b^* values are in the same order of magnitude, the a^* value of our sample is much higher, leading to a material much redder than the reddest 18-K gold alloys (5 N).

Spectral curves of standard gold alloys provided by Varinor (Delémont, Switzerland) are presented in Fig. 5. It is worth noting that the spectral curves of all the traditional coloured gold are very similar even though a real difference can be observed macroscopically. For our developed 18-K red gold, the reflectance is much lower. This can be partially attributed to the fact that the sample is neither polished nor brushed. However, we can notice that for the same material, the surface state (polished or brushed) does not modify radically the shape of the spectral curve. In our case, in between 370 and 480 nm, the spectral curve is flat and has a reflectance of about 5 % whereas for regular gold, this value is comprised between 30 and 48 % in the same wavelength range. From 500 to 680 nm, the reflectance increases linearly from 4 to 22 % whereas traditional gold are characterized by a bump in the same wavelength range.

Figure 6 is a picture of our 18-K red bulk gold.

Conclusion

We report in this study a new way to obtain deeply coloured gold materials using the surface plasmon resonance effect of gold nanoparticles. The resulting colour is markedly different from the one of traditional alloys. Thanks to our method, an entirely new range of coloured gold can be obtained, with much deeper colours than traditional gold alloys.

We also can obtain a deeply red 18-K bulk piece of gold, whose aspect is radically different from traditional gold. Our red gold is much redder than the reddest 18-K gold on the market. The gold content is measured using EDX and the cupellation technique. Both techniques demonstrate that the gold rate of the pieces is higher than 75 %. To our knowledge, this is the first example of a deeply coloured piece of gold with a gold rate higher than 75 % and made using the nanotechnology approach.

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