

Comparative study of the tarnishing resistance of several coloured base gold alloys

Carvalho, O.¹, Soares, D.¹, Fonseca, A.², Silva, F.S.¹

¹Department of Mechanical Engineering, University of Minho, Azurém, 4800-058 Guimarães, Portugal

²Department of Chemistry, University of Minho, Campus of Gualtar, 4700-057 Braga, Portugal

Abstract

The stability of coloured gold alloys may be dependent on the environment that involves them. This paper is concerned with the effect of an artificial sweat solution in the stability of several gold base alloys with different colours. The changes in the samples physical properties, colour, brightness, and reflectance were measured for several periods of immersion.

Two types of alloys (purple and blue coloured alloys) showed to be sensitive to the artificial sweat solution. The other tested alloys have a high resistance to tarnishing comparable with the results obtained for pure gold.

Keywords: coloured gold alloys, tarnishing, corrosion, artificial sweat.

Introduction

Gold have good chemical and physical characteristics, like stability, electrical and thermal conductivity, bio-compatibility [1], that allow it to be used in many applications. As an example of his large variety of applications in particular jewelry [2]. Actually, with the advances of nanotechnology, this metal is also starting to be used in this field [3].

However, in certain environmental conditions and in certain gold alloys there may be some surface degradation with change in colour and brightness (tarnishing). Some environments like transpiration and chloride containing solutions are propitious to promote the tarnishing on surface of gold based alloys [4, 5]. Some alloys are more prone to tarnishing than others. Purple gold and blue gold showed some susceptibility to corrosion of surface, as mentioned in some articles [1]. However the tarnishing effect in some alloys is usually presented, in the literature, in a qualitative way. In this work the susceptibility to tarnishing of several gold base alloys is studied for different immersion times in an artificial sweat solution. The alloy surface changes, in terms of colour, brightness and reflectance, are quantified (CIELAB system) and compared with a reference material (pure gold).

Experimental procedure

In this work 8 gold based alloys were used in order to compare their surface stability. The alloys chemical composition is presented on Table 1 with the indication of the initial colour. The samples were prepared by melting from the pure elements ($\geq 99.9\%$) in an inert atmosphere, except for sample N° 5 where a base alloy (WG alloy) was used to produce the white colour. Sample N° 8 is pure gold and will be used as a reference material for the analysis of the tarnishing effects on the other alloys.

Table 1– Alloys chemical composition (wt%) and initial colour of the samples used in this work.

Element	Sample N°							
	1	2	3	4	5	6	7	8
Au	80	80	80	80	80	79	46	100
Ag	10	20	-	2	-	-	-	-
Cu	10	-	20	-	-	-	-	-
Pd	-	-	-	18	-	-	-	-
WG alloy*	-	-	-	-	20	-	-	-
Al	-	-	-	-	-	21	-	-
In	-	-	-	-	-	-	54	-

Alloy colour yellow green red white white Purple blue yellow

WG alloy* - base alloy to produce white gold in industrial conditions

The samples used in this work were immersed in an artificial sweat solution in order to study the superficial physical stability, namely colour and brightness.

The chemical composition of artificial sweat (in wt %) was [6]: 0.5 % sodium chloride; 0.1% lactic acid; 0.1 % urea and deionized water to make 100%. The surface sample physical characteristics were measured after the following selected immersion times: 1 hour, 1 day, 5 days, 9 days and 18 days.

For the experimental tests, each sample was placed (face up) in a container bottom with a constant amount of 50 mL of solution. Before the immersion tests, the sample surface test was grinded and polished until a final particle diameter of 1 μ m. The sample initial weight varies between 1,4427 and 2,5039 g and the surface analysis diameter varies between 9-10 mm. The samples containers were placed on a water-bath at 37 ± 2 °C in order to simulate the temperature of human body. During the tests, the containers were capped to prevent the solution evaporation [7].

The volume of solution, the solution pH, the exposure time, the mass of sample and solution temperature were controlled after each period of immersion.

At the end of each selected test period (one hour, 24 hours, 5 days, 9 days and 18 days), the samples were removed from the solution, washed with distilled water [8], cleaned ultrasonically in ethanol and then dried [4, 9].

The change of colour due to modification of surface, as result of the reactions between the sample and the solution (tarnishing effect), was measured using a computerized spectrometer (CIELAB system) [1, 7, 8]. The sample surface colour change is described in equation 1:

$$DE^* = ((L_2^* - L_1^*)^2 + (a_2^* - a_1^*)^2 + (b_2^* - b_1^*)^2)^{1/2}$$

where L^*1 and L^*2 are the brightness values before and after the test, respectively; a^*1 and a^*2 are the red-green colour values before and after test, respectively; and b^*1 and b^*2 are the yellow-blue colour values before and after the test, respectively.

Results and discussion

Samples changes (after the 18 days of immersion) in terms of weight loss, solution pH variation and colour difference (ΔE^*) are presented in Table 2. The evolution of the colour change with the immersion time, for all samples, is presented in figure 1.

Using sample 8 as a reference material (pure gold with high resistance to tarnishing [4]) it is concluded that only on samples 6 and 7 there is a significant change in colour and weight. On samples 1, 2, 3, 4, 5 the colour and weight changes are comparable to the one obtained in the reference material.

Table 2 – Total weight loss, solution pH variation and colour difference (DE^*) obtained in all samples after the 18 days of immersion in artificial sweat.

Samples	Weight lost (g)	Solution pH variation	Colour difference (DE^*)
1	0,0014	0,11	1,75
2	0,0004	0,08	1,60
3	0,0008	0,10	2,81
4	0,0003	0,10	1,17
5	0,0013	0,30	0,58
6	0,0101	1,81	42,51
7	0,0171	1,07	7,85
8	0,0002	0,11	2,78

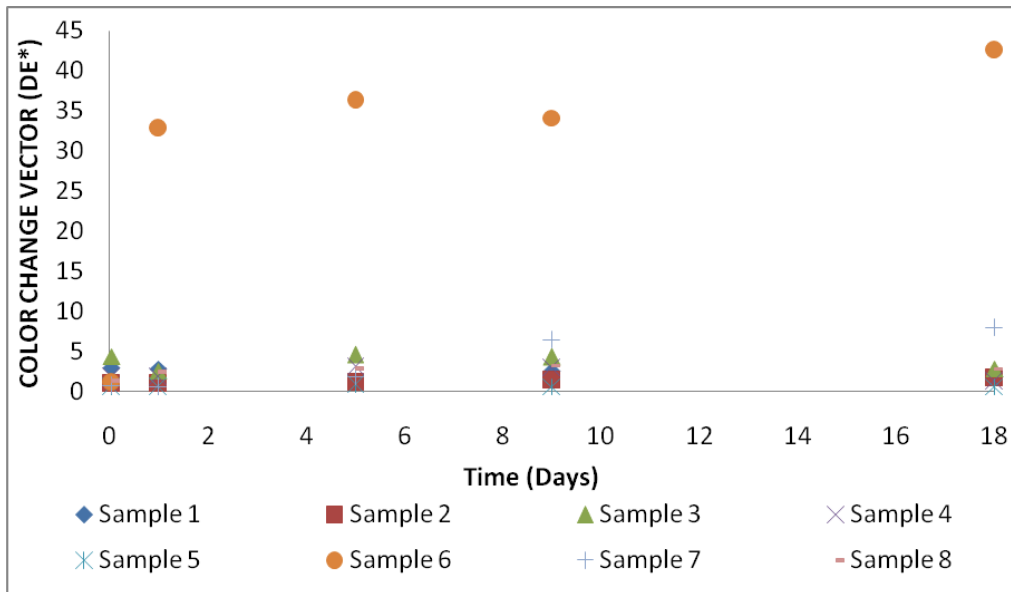


Figure 1 - Evolution of colour change vector (DE*), of all samples, with the immersion time in artificial sweat.

As presented in figure 1 only for samples 6 and 7 a significant change in the physical properties were detected in the immersion tests in artificial sweat. The obtained results will be presented with more detail for those alloys.

Purple colour alloy: sample 6

A sample total weight loss of 0.0101 g was obtained (Table 2).

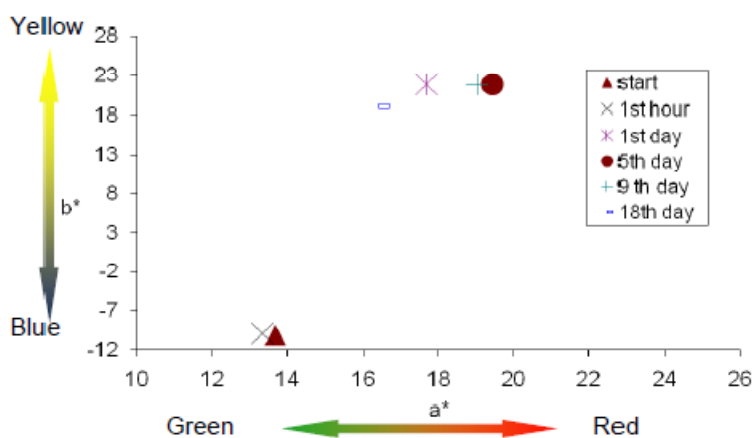


Figure 2 – Evolution of a* and b* values on sample 6 along the several periods of time of immersion in artificial sweat.

The surface modifications promoted significant changes in the samples colour, brightness and reflectance. Figure 2 present the changes in sample colour with the immersion time. The sample colour changes from purple to a pale red, corresponding to an increase in the yellowish component. The colour changes were more significant between the first hour and the first day of immersion (Fig. 2).

A substantial variation of reflectance and brightness (L^*) also occurs during the immersion tests . The brightness changes occurred especially between 1 hour to 1 day and after 9 days of immersion. During these periods the brightness decrease especially in last period previously indicated.

The sample reflectance changes especially in the lower wave lengths mainly during the first 24 h of immersion time. Between the 9th and 18th day of immersion reflectance starts to decrease in all wave lengths.

Blue colour alloy: sample 7

Sample 7 also presents changes in the sample colour, brightness and reflectance, in the immersion tests. However these changes are much lower than those obtained in sample 6 (Fig. 1).

A sample total weight loss of 0.0171 g was obtained (Table 2).

The values (a^* and b^*) of colour, does not substantially change with time (Fig. 3). However there are changes mainly in brightness and reflectance, decreasing during the whole test being more significant after day 5.

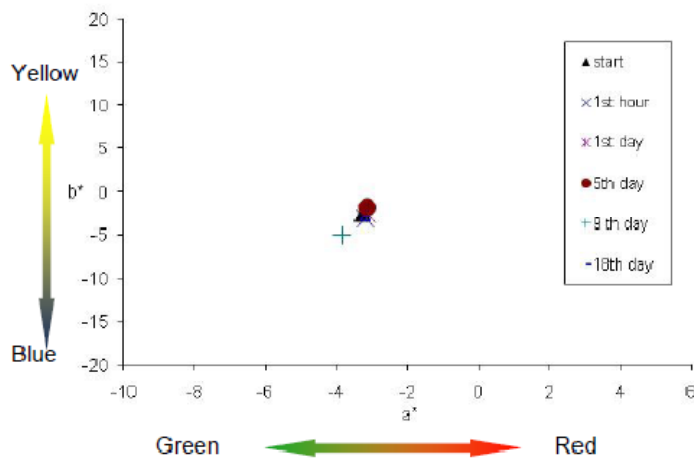


Figure 3 – Evolution of a^* and b^* values on sample 7 along the several periods of time of immersion in artificial sweat.

The global colour modification (DE^*) has a smooth change during the all test but with an accentuated slope after day 5.

Conclusions

The surface stability of several coloured gold alloy was studied for several times of immersion in an artificial sweat solution. The sample surface changes were determined in terms of surface colour and brightness with the immersion time.

Samples 1, 2, 3, 4 and 5 don't have significant changes of colour and brightness. These alloys have a superficial stability comparable to the pure gold (sample 8). In opposite, samples 6 and 7 presented significant changes in the superficial state and in related colour and brightness.

On sample 6, significant changes in terms of colour and brightness immediately after 1 day of immersion.

On sample 7 significant changes in terms of colour and brightness occurred after 5 days of immersion.

Comparing sample 6 and 7 it was concluded that the first one is more sensitive to the tarnishing effect. This behaviour occurs faster and in a more severe scale in that alloy.

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