P Rattanapoltee and P Thongnopkun*
Gems and Jewelry Research Unit, Faculty of Gems, Burapha University, Chanthaburi Campus, Chantaburi, 22170, Thailand

*E-mail: pimthong@go.buu.ac.th

Abstract. Silver is a promising precious metal for the jewelry industry. The silver jewelry findings exposed to air would be tarnished because it comes into contact with sulfur particles in atmospheres. Therefore, surface treatments and coating methods were developed to prevent the tarnishing of silver. However, the methods still have several limitations and disadvantages. The objective of this research was to develop gold microplates for surface coating and tarnish resistance of silver. In this study, the gold microplates were synthesized by chemical reduction methods. Multilayer gold coating was performed by a simple dip coating method to produce the gold film using a gold microplate solution, which disperses gold particles in ethylene glycol. The anti-tarnish properties of the coated silvers were investigated using the sodium sulphide solution. To specify the color change after multilayer coatings of gold particles and tarnishing test, the color measurement was determined according to the Commission Internationale d’Eclairage (CIELAB) standard by UV-visible spectrometer. The result pointed out that the gold microplates layers coating on silver are invisible and efficiently prevents tarnishing.

1. Introduction
Silver is a well-known precious metal and most commonly used in the metal industry. The tarnishing is a reputed problem for silver causing by sulfur reaction, either from the perspiration or surrounding air [1-3]. It reacts with the silver surface and forms silver sulphide. Accordingly, the surface of the silver initially becomes discoloration and causes a destructive effect on its luster. Although atmospheric tarnishing of silver is a major problem, however, there is a limited study on using surface treatments to confer tarnish resistance. Some surface treatments include metallic coatings by electroplating, such as coatings of Ni, Rh, Pt, Ir, and Pd, are complicated and little performance data are available [4-5]. Physical vapor deposition (PVD) is another capable technique for transparent coatings of Al, Zr, Mg, Ti, and Nb oxides, which can be deposited by reactive sputtering. However, PVD is an expensive and complicated process [4]. In addition, it presents intrinsic defects that can affect the corrosion behavior [5]. There are several coatings based on organic materials [6], using especially for storage and silverware. However, the organic films are normally visible and not sufficiently protect in the case of high thickness. Thus, this research aims to present an alternative simple coating process for tarnishing resistance of the silver metal. The gold microplate was used as a coating material, due to it is one of the chemically inert metals and also does not tarnish. The small amount of gold microplates is being applied with the simple dip coating process; therefore, the technique is affordable and could be useful for some applications in industry. The article focused on the effect of the number of dip coating and color variation of silver after coating and tarnishing test.
The surface morphology and chemical analysis of silver surface employed via SEM-EDS and color change were provided by using CIELAB measurement.

2. Experiment

2.1. Synthesis of gold microplates

The gold microplates were synthesized by the reduction of a 0.7 M tetrachloroauric acid (HAuCl₄). It has been initiated by 0.35 mM polyvinylpyrrolidone (PVP) using 6.0 M ethylene glycol (EG) as a stabilizer, shown in figure 1(a). Deionized (DI) water was used to prepare the aqueous micellar solution and to rinse the samples in the experiments. The SEM image showed various shapes of synthesized micrometer-sized gold particles approximately 6-10 micron, as shown in figure 1(b).

2.2. Substrate preparation and coating by a dip coating technique

Substrates are fine silver plates (99.5% pure) cutting into coupons with the dimension of 1×1×0.2 cm. Before coating with gold microplates, the samples were polished with SiC paper up to 600 and 2000 grade, and then soaked with DI water in the ultra-sonicate bath for 5 min followed by degreasing with acetone. For dip coating procedure, the silver samples were immersed into an aqueous gold microplate solution containing 10 mL DI water, 1 mL EG, 0.1 g PVP and 1 mL of 0.1 mol/L gold microplate solution during 5 min at room temperature. The monolayer coated silver in the gold solution was repeated 2 and 3 times in order to obtain the double layer and trilayer coatings, respectively (table 1).

Upon removal, the samples were dried, and then anneal at 400 ºC in the electronic oven to eliminate the organic species and sintered gold microplates on the silver surface.

Table 1. Sample names and coating conditions.

| Sample names | Coating with gold microplate | Number of dip coating (times) |
|--------------|------------------------------|------------------------------|
| S0           | -                            | 0                            |
| MS1          | ✓                            | 1                            |
| MS2          | ✓                            | 2                            |
| MS3          | ✓                            | 3                            |

2.3. Data acquisition

The surface morphology and chemical analysis were obtained using JEOL JSM-6510A SEM-EDS. USB4000-Ocean Optics UV-VIS spectrometer (D65 light source, observe the angle of 10°) was employed for color calculation following CIELAB standard. CIELAB color space describes all the colors visible by three coordinates in terms of L*, a*, and b*: L* for the lightness from black (0) to white (100), a* from green (-) to red (+), and b* from blue (-) to yellow (+). The measurements were carried out in reflectance mode with wavelength ranging from 300 nm to 800 nm at a scan speed of 100 nm/min. For data comparison, the color difference (ΔE*) was measured before and after coating with gold microplates, and also after tarnishing test using, ΔE* = (ΔL² + Δa² + Δb²)¹/₂.

2.4. Tarnishing test

Sodium sulphide nanohydrate (Na₂S·9H₂O) aqueous solution was used as a quick estimate for tarnishing test. As prepared at 25 ºC the pH was measured to be 4.8. Tarnish tests were performed in a sulphur vapor atmosphere produced by the 0.1% sodium sulphide solution for 0, 15, 30, 45, and 60 min. The chamber was closed to prevent rapid and extensive evaporation of sulphides. For the color difference, a well-polished, as-cast silver sample (0 min test) was used as a reference specimen.

3. Results and discussion

3.1. Visual appearance and color measurement
Basically, the visual appearance of the coating is related to color and gloss correspondingly to the material formulation, coating thickness, and morphology. The visual appearance of mono-coated and double coated samples reveal similar to those of uncoated silver plate. The trilayers coated silver exhibit slightly different yellow color reflecting from the silver surface. The CIELAB color measurement was employed via UV-Visible spectrophotometer in order to investigate the color change after gold coating. The alteration of the coordinates a* and b* are reported in trends of the absolute value shown in the graphs of figure 2. Considering at a* and b*, the color of coated material turn to more greenish-yellow after modified with mono and multilayer coating however it was difficult to discern by naked eyes. On the other hand, it appears yellow when treated with trilayers gold microplates and can be easily observed. The appropriate coating could be as thin as possible to avoid the degrading of the attractive surface appearance of silver. Thus, the trilayers coating in the present study is not suitable for silver coating yet. In the case of lightness, L* was decreased when the number of the coating was increased, as shown in figure 3(a) (0 min test). Therefore, it affected the color difference (ΔE*) of the silver after the coating processes. The ΔE* value was higher after the number of the coating was increased, as reports in figure 3(b) (0 min test).

Figure 2. The a*b* coordinate of uncoated and coated silver by gold microplates.

Figure 3. (a) Change of L*; and (b) ΔE* of silver sample before coating (S0; 0 min), after coating (MS; 0 min) and after tarnishing test (S0 and MS; 15-60 min).

3.2. SEM analysis
The morphology of uncoated and coated silver with different condition was investigated by means of the SEM, as shown in figure 4. SEM image of the uncoated silver plate shows a low roughness surface. The sequence of images shows the surface of silver covered with mono, double and tri-coating gold microplate, respectively. The monolayer and double layer coating slightly reveals a thin layer of gold microplate deposited on the silver surface. As expected, the SEM image of trilayers coating discloses the zone of a gold microplate on the surface seen as hexagonal and truncated triangular shape. It was confirmed that the thin layer of gold microplates can be deposited on the silver surface. The increasing of the coating layer is evidenced by the EDS spectrum. It is possible to see the relative increase of gold and sulphur content after coating and tarnish test, respectively (figure 5).

3.3. Tarnishing test
The results of tarnishing test of the uncoated and coated silver under an atmosphere of 0.1% Na₂S are shown in table 2. The anti-tarnish properties were improved proportionally to the increasing number of gold microplate coating. The CIELAB color method was performed in order to characterize the color and color change, after gold coating and tarnishing test. Regarding the L* and ΔE*, effects of gold microplate coating on the measured color are shown in figure 3. A lower ΔE* and higher L* value indicates better tarnish resistance.
Table 2. Color change after tarnishing test.

| Sample | Testing time (min.) |
|--------|---------------------|
|        | 0       | 5       | 10      | 15      | 30      | 60      |
| S0     | S0      | S0      | S0      | S0      | S0      | S0      |
| MS1    | MS1     | MS1     | MS1     | MS1     | MS1     | MS1     |
| MS2    | MS2     | MS2     | MS2     | MS2     | MS2     | MS2     |
| MS3    | MS3     | MS3     | MS3     | MS3     | MS3     | MS3     |

4. Conclusion

The gold microplates were synthesized and modified on a silver plate substrate by dip coating to improve the anti-tarnish properties of silver. In the present study, the coating process can form a complete anti-tarnishing gold film showing in SEM images. However, CIELAB color measurement indicated that the number of coatings affects color variation. An increasing number of coatings trend to reveal yellowish gold reflection on the sample surface which can be observed by the naked eyes.

After the tarnish test, all condition of gold microplates coated on the silver substrate can improve the anti-tarnishing properties. Therefore, the present results confirm that mono and double layer coating are optimizing condition and effectively for modifying the surface, invisible and preventing the silver surface from tarnishing.

Acknowledgments

The authors gratefully acknowledge Burapha University Research Grant No. 148/2558 for financial support. In addition, the authors sincerely thank Miroscopic center, Faculty of Science, Burapha University, Thailand, for SEM-EDS analysis.

References

[1] Kim H 2003 Mater. Corros. 54 243
[2] Hallett K, Thickett D, McPhail D S and Chater R S 2003 Appl. Surf. Sci. 203 789
[3] Grissom C A, Grabow N, Riley C S and Charola A E 2013 J. Am. Inst. Conservat. 52 82
[4] Paussa L, Guzman L, Marin E, Isomaki N and Fedrizzi L 2011 Surf. Coat. Technol. 206 976
[5] Vacandio F, Massiani Y, Eyraud M, Rossi S and Fedrizzi L 2001 Surf. Coat. Technol. 137 284
[6] Gay PA, Bercot P and Pagetti J 2004 Plat. Surf. Finish. 91 71