The Fabrication of Au-coated Ag Calibration Standards for Determination of Coating Thickness by X-Ray Fluorescence Spectrometry

Montira Seneewong-Na-Ayutthaya [1], Narong Praphairaksit [1]
Jakraphan Suwanvijit [1], Somchai Manuskiattikul [2],
Thidarat Muangthai [1], Pichaya Akkaranurukkul [1] and Prowtawun Tunprainich [1]

1 *The Gem and Jewelry Institute of Thailand (Public Organization)*
2 *Umicore Precious Metals (Thailand) Ltd.*

Electroplating is considered one of the most important processes in the silver jewelry manufacturing. The silver (Ag) jewelry is often coated with gold (Au) to produce a shiny surface as well as to prevent tarnish and corrosion in order to increase its value. The thickness measurement of coated jewelry is a necessary protocol to comply with the quality standard of global trade requirement. X-ray fluorescence spectrometry (XRF) has been recognized for its application in measuring coating thickness in the worldwide jewelry industry. XRF requires the use of coating thickness calibration standards as a reference material to ensure that the determination is accurate and reliable. This research was aimed to fabricate an electroplating kit to prepare Au-coated Ag calibration standards with coating thickness ranging from 0.5 to 5.0 μm for 18K and 24K gold-plated samples. The result showed that the reproducibility of coating thickness was dependent on the sample area calculation, current density, temperature, rotating speed, and plating time during the electroplating process. This study has been accomplished by the thickness calculation through certain formula, XRF analysis, and cross-section measurements obtained by scanning electron microscopy (SEM). XRF mapping was also used to test the homogeneity, reproducibility, and uncertainty of the coating layer. As a result, the uncertainty value of the prepared Au-coated Ag is efficiently constrained regarding the certified calibration reference material. The Au-coated Ag calibration standards from this research were successfully demonstrated as trustworthy reference materials for XRF analysis and suitable for commercial uses in order to reduce the costly expenses associated with the normally imported standards.

Keyword: Coating thickness calibration standard, Electroplating, Silver, Gold, X-ray fluorescence (XRF)

Method

For this study, the electroplating process is the deposition of a gold coating onto a round silver plate (surface area = 6.28 cm2). The process includes three main steps, consisting of (1) surface pretreatment, (2) electroplating process, and (3) cleaning after plating. The setup of the electroplating station is presented in Figure 1. The prepared Au-coated Ag calibration standards with coating thicknesses from 0.5 to 5.0 μm are shown in Figure 2. The conditions for 18K and 24K gold electroplating are given in Table 1. Afterthat, the prepared Au-coated Ag samples were compared with certified calibration reference materials considering their uncertainty values from XRF analysis.

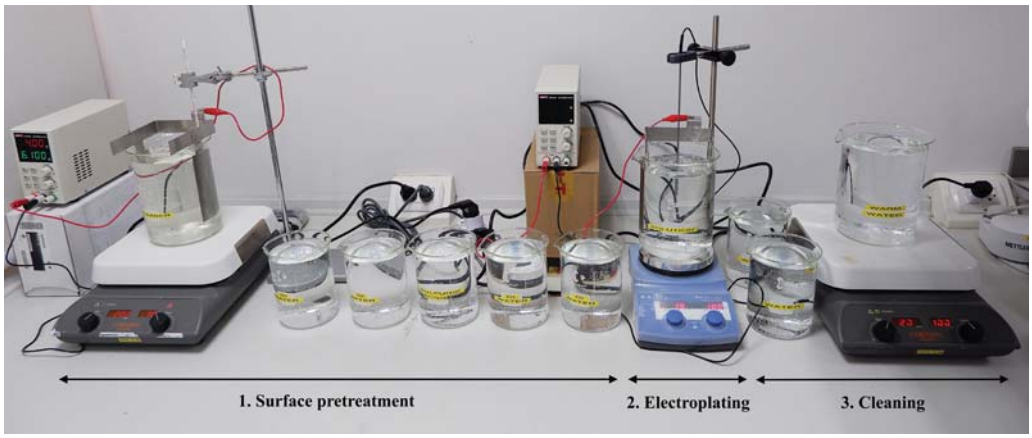

Figure 1 : The electroplating kit to prepare for Au-coated Ag calibration standards

Figure 2 : Au-coated Ag calibration standards from 0.5 to 5.0 μm (top) 18K and (bottom) 24K gold-plated samples

Table 1 : Electroplating conditions for Au-coated Ag samples

Table 1. Electroplating conditions for Au-coated Ag samples

Conditions	18K Au-coated Ag	24K Au-coated Ag
Step 1 *Surface pretreatment by electrocleaning*		
Voltage	4 V	4V
Temperature	60-70 °C	60-70 °C
Rotating speed	70 rpm	70 rpm
Step 2 *Electroplating process*		
Electrolyte type	Alkaline - cyanide	Non-cyanide
Coating characteristic	Alloy: gold-silver	Fine gold
Coating color	Green-yellow	Yellow
Density of the coating	Approx. 15.5 g/cm^3	Approx. 19 g/cm^3
pH-value	>11	5.8 – 6.2
Current density	0.063 A	0.0315 A
Temperature	30-40°C	50°C
Rotating speed	170 rpm	170 rpm
Step 3 *Cleaning*		
Temperature	70-80°C	70-80°C

Results and Conclusions

As shown in Table 2, three measuring values for the thickness of metal coatings by different techniques, i.e. XRF, coating weight calculation (non-destructive methods), and mechanical cross-sectioning (destructive method) were used to evaluate all plated samples. The thickness can be extrapolated from XRF and calculation data. The cross-section is an accurate technique which allows for a direct measurement of the depth and thus used for the verification of a thin-film thickness. The cross-section analysis process consists of two steps: sample preparation (cutting the sample in half) and transversely observing along the layer thickness through a SEM as shown in Figure 3, showing the representative of 18K and 24K Au-coated samples. All prepared 0.5 to 5.0 µm Au-coated Ag calibration standards yield a consistent average thickness, this produced uncertainty values obtained by XRF calculation are similar to those of the imported calibration standards. Wherewith, the uncertainty value indicates the error analysis as a result of the homogeneity and stability of materials.

Table 2 : Results of coating thickness measurement and uncertainty

Samples	Plating time	Thickness measurement (µm)			Uncertainty
		XRF	Coating weight calculation	Cross-section	
18K_0.5 µm	58 s	0.50	0.50	0.55	-
18K_1.0 µm	1 min 50 s	1.03	0.97	1.46	-
18K_2.0 µm	3 min 40 s	2.03	1.97	2.66	-
18K_3.0 µm	5 min 30 s	3.03	2.99	3.25	-
18K_5.0 µm	9 min 10 s	5.02	5.12	5.88	-
24K_0.5 µm	2 min 2 s	0.50	0.52	0.58	± 0.02
24K_1.0 µm	4 min 2 s	1.02	1.01	1.25	± 0.03
24K_2.0 µm	8 min 4 s	2.05	2.08	2.04	± 0.03
24K_3.0 µm	12 min 6 s	3.05	3.03	3.70	± 0.05
24K_5.0 µm	20 min 10 s	5.03	5.06	5.88	± 0.18
24K_01RM*	-	0.52	-	-	±0.02
24K_02RM*	-	0.95	-	-	±0.03
24K_03RM*	-	2.93	-	-	±0.04
24K_04RM*	-	5.56	-	-	±0.02
*RM = Reference Material					

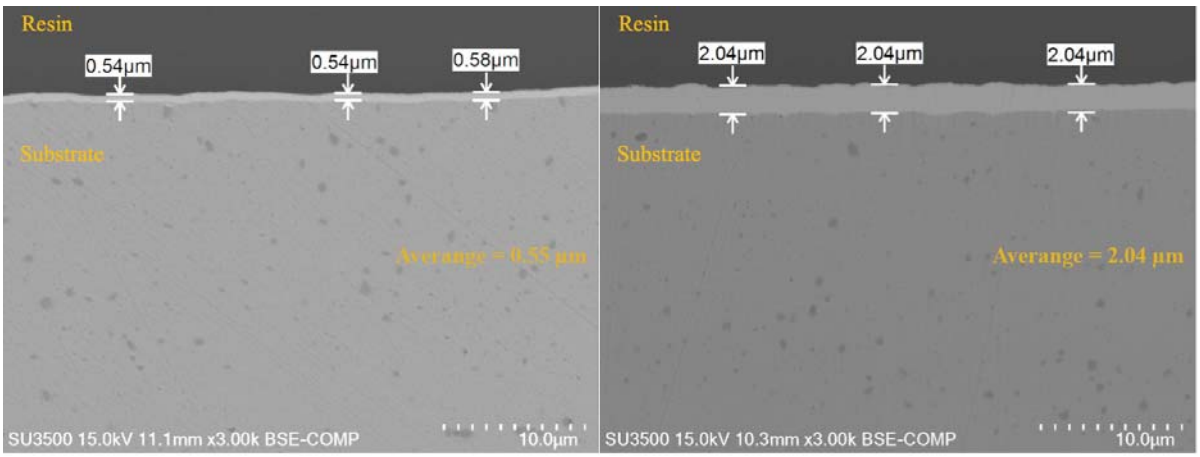

Figure 3 : SEM images showing the morphology and thickness of Au coating onto Ag plates (left) 18K_0.5 µm and (right) 24K_2.0 µm samples with a magnification of 3000X

Acknowledgment

This project was funded by the Thailand Science Research and Innovation (TSRI).

References :

Brepohl, E., (2001), The theory and practice of goldsmithing, New York: Brynmorgen Press.

Chalumeau, L., Wery, M., Ayedi H. F., Chabouni, M. M., Leclere, C., (2006), Development of a new electroplating solution for electrodeposition of Au-Co alloys, Surface and Coatings Technology, Vol. 201, N. 3–5, pp. 1363-1372.

Fan T., Zhang H., Shang P., Li C., Chen C., Wang J., Liu Z., Suganuma K., (2017). Effect of electroplated Au layer on bonding performance of Ag pastes. Journal of Alloys and Compoumds, Vol. 731, pp. 1280-1287.

Giurlani, W., Zangari G., Gambinossi, F., Passaponti, M., Salvietti, E., Benedetto, D.F., Caporali, S., Innocenti M., (2018), Electroplating for decorative applications: recent trends in research and development, Coating, Vol. 8, No. 260, pp. 1-25.

Giurlani, W., Berretti E., Innocenti M., Lavacchi A. (2019)., Coatings thickness determination using x-ray fluorescence spectroscopy: monte carlo simulations as an alternative to the use of standards. Coating, Vol. 9, No. 79, pp. 1-11.

Giurlani, W., Berretti, E., Innocenti, M., Lavacchi, A., (2020), Measuring the thickness of metal coatings: A review of the methods, Coating, Vol. 10, pp. 1-36.

Sokolov A., Hasikova J., Pecerskis A., Gostilo V., Lee K.Y., Jung H., Lim J.H., (2018), Application of industrial XRF coating thickness analyzer for phosphate coating thickness on steel. Coating, Vol. 8, No. 126, pp. 1-10.