

RHODIUM PLATINGS – EXPERIMENTAL STUDY

Recived – Prispjelo: 2012-06-17
Accepted – Prihvačeno: 2012-12-15
Preliminary note – Prethodno priopćenje

Modern rhodium plating solutions are based on either sulphate or phosphate. Although in theory there are four possible combinations, in practice only three different rhodium electrolytes are used. These are based on dilutions of rhodium sulphate or phosphate concentrates with added sulphuric or phosphoric acid.

These processes are be discussed in this paper with a demonstration of Rh platings in the Slovenian firm Zlatarna Celje d.d..

Key words: rhodium, plating, jewellery, properties

INTRODUCTION

Rhodium plating has enabled the basis of commercial process since the early 20th century. Literature [1] from that time reported that rhodium could be deposited, not only from the double chloride with alkali metals or ammonium, but more effectively from rhodium sulphate, with a relatively large excess of sulphuric acid being required to prevent hydrolysis of the rhodium sulphate. Rhodium (Rh) is electrodeposited for either decorative or functional purposes [2, 3]. There are two major processes, which are the sulphate and phosphate based electrolytes respectively. With the consideration that Rh belongs to the platinum group of metals, it is extremely corrosion resistant. Rhodium deposits are rare and not found in high concentrations. Moreover, the price of Rh is high. Typically, use of Rh is in decorative plating on jewellery of all types, for its intensely white colour, which is whiter than the very best silver deposit. Rh electrodeposits are very hard with high abrasion resistance. Rh is also non-tarnishing, and for this reason is it used as a protective flash coat on silver surfaces. Another use of rhodium is to flash plate precious stone settings and mounts [4,5] so giving them greater brilliance. Rh deposit is still the most widely used contact surface on reed switch contacts, because of its resistance to wear and arc damage, allied with its acceptable electrical contact resistance values [6].

PHYSICAL AND CHEMICAL PROPERTIES OF RHODIUM

Some key properties of Rh are: density: 12,41 g/cm³, melting point 1 966 °C, boiling point 3 727 °C, heat conductivity 150 W/mK (at 20 °C), electrical resistivity 4,34 μΩ/cm, hardness 120 HV annealed 300 HV wrought and 800 - 1 000 HV for electro deposits [7]. If we look at chemical resistance, Rh is very resistant to acidic attack: to massive metal in insoluble in aqua regia, hot concentrated HCl and HNO₃, but it dissolves in hot concentrated H₂SO₄ and also in fused KHSO₄. Rh has the electronic configuration 2 -8 -18 -16 -1, and the only valence states of any consequence are +1 and +3 [8]. For all practical purposes, Rh electrolytes are based solely on +3 valence compounds.

CHEMISTRY AND ELECTROLYTE TYPES

Rhodium chloride, RhCl₃, is by far the most commonly used compound; the soluble form may be prepared from basic rhodium chloride or rhodium hydroxide by adding hydrochloric acid, to produce rhodium chloride tri-hydrate or tetra-hydrate. Rh is dissolved in strong sulphuric acid (of boiling point cca 250 °C) by refluxing until the Rh is converted into rhodium sulphate solution [9]. In practice the concentrate is diluted, excess alkali added to precipitate rhodium hydroxide. This precipitate is then re-dissolved in sulphuric acid to yield a dark red rhodium concentrate of nominal composition Rh₂(SO₄)₃, which can be adjusted to a concentration of, typically, 100 g/l Rh and with a specific small excess of sulphuric acid. This concentrate is then used to prepare plating solutions. In a manner similar to the sulphate, rhodium hydroxide is dissolved in ortho-phosphoric acid to produce rhodium phosphate concentrate containing some free acid [10]. The metal content is

R. Rudolf, I. Ivanič, Faculty of Mechanical Engineering, University of Maribor, Maribor, Slovenia, B. Budič, Naional Institute of Chemistry, Ljubljana, Slovenia, D. Stamenković, School of Dental Medicine, University of Belgrade, Belgrade, Serbia, M. Čolić, Medical Faculty of the Military Medical Academy, University of Defence, Belgrade, Serbia, B. Kosec, Faculty of Natural Sciences and Engineering, University of Ljubljana, Ljubljana, Slovenia

usually adjusted to 100 g/l Rh. Modern rhodium plating solutions are based on the sulphate or phosphate. In theory there are four possible combinations, in practice only three different rhodium electrolytes are used. They are based on dilutions of rhodium sulphate or phosphate concentrates with added sulphuric or phosphoric acid [11].

i) $\text{Rh}_2(\text{SO}_4)_3$ concentrate plus sulphuric acid – used for decorative purposes, the metal content is typically Rh 2 g/l and free sulphuric acid concentration is 30 - 50 g/l. Processes based on this type of electrolyte are usually used for deposits from 0,05 μm upwards, but seldom for deposition of thickness $> 0,2 \mu\text{m}$.

ii) $\text{Rh}_2(\text{SO}_4)_3$ concentrate plus phosphoric acid – typically Rh 2 g/l plus added free phosphoric acid at 30 - 50 g/l. This electrolyte and the following are used predominantly for thin decorative deposits.

iii) Rh_2PO_4 concentrate plus sulphuric acid - typically Rh 2 g/l plus added free sulphuric acid at 30-50 g/l. This is effectively the same electrolyte as (ii), the free acid content being a mixture of sulphuric and phosphoric acids, depending on how the solution equilibrates. The ratio of free sulphuric acid to free phosphoric acid is not of great importance, but it is generally maintained at or above 1.

iv) Rh_2PO_4 concentrate plus phosphoric acid - typically Rh 2 g/l plus added free phosphoric acid at 30 - 50 g/l. This is the most widely used decorative plating electrolyte, with cathode efficiency below 10 %. This has a considerable benefit when a low deposit thickness (e.g. 0,1 μm Rh) is required for decorative plating, since any excess plating time will involve minimal excess Rh consumption. This is always important when cost control is imperative.

The most important fact is that Rh- plating solutions are not diluted with water alone and could be prepared from a high concentration, usually at 100 g/l (or less often 50 g/l), of Rh. Such solutions do not contain sufficient free acid to prevent hydrolysis when diluted only with water and precipitation of yellow rhodium hydroxide will occur invariably as a result. The strongly acidic electrolytes used for rhodium plating may lead to chemical attack on the substrate, or immersion (displacement) coating of surfaces. Simple Rh plating formulations have no inherent brightening properties, for a bright finish the article must be bright or have been plated using a bright undercoat process. Because cathodic current efficiency is always relatively low, substantial amounts of hydrogen are released at the cathode and there is a risk of gas pitting or at least of gas bubble marks forming, unless the cathode rod movement is adequate. All rhodium processes include insoluble anodes, usually platinum coated titanium mesh [12]. In the laboratory pure Pt wire or foil may be more readily available.

The temperature of the solution is very important. For decorative flash plating it is helpful at 40 - 45 °C so that evaporative losses allow for return of larger quanti-

ties of drag-out rinse to the process bath. However, working at 20 - 25 °C will mean lower heating costs, a slower plating rate and a higher voltage as the bath conductivity will be lower. In many cases this is a worse option.

It is known that simple rhodium sulphate processes, i.e. without additives of any sort, give highly stressed deposits and it suggests there is a limiting thickness, typically about 2,5 - 5 μm , above which cracks form [13]. This process plays an important role in innovation from perspective of organisations and widely to generate new value [14,15].

EXPERIMENTAL WORK

We prepared plate substrates from Ag-Cu (Ag 925 purity) for rhodium plating. Their dimensions were 20 mm \times 10 mm and 2 mm in thickness. This material was chosen for the reason that the chemical composition is very near to the composition of silver jewels [16]. The experiments were carried out according to the above-mentioned combination (i) - see previous section. For this purpose, we used new chemicals and cleaned instruments. We tested the optimal time of Rh plating. According to this the selected times were: 1 min, 3 min and 5 min. The other technological parameters were the same for all experiments ($T = 50 \text{ }^\circ\text{C}$ -temperature of bath, 2 - 3 V voltage, 0,2 A current, Pt cathode in meshed form) [17,18]. The tested substrates were connected on the position of anode.

Auger Electron Spectroscopy (AES) (Microlab 310-F from THERMO Scientific with field emission electron gun FE) and X-ray Photoelectron Spectrometry (XPS) were used to characterize the surface of the Rh galvanised substrate. The primary electron beam was used at a current of 10 nA and kinetic energy of 10 keV giving the resolution of 10 nm. The samples were cleaned with Ar^+ ions ($E = 2 \text{ keV}$, $r = 12 \text{ mA cm}^{-2}$, $Q = 47$) to remove surface contaminants. The XPS analysis was performed after the sample was sputtered with Ar^+ 3 keV for 5 min. For depth profiles, the samples were sputtered with a 3 keV Ar^+ sputter rate of about 1,2 nm/min and the analysis was performed before the first sputtering and after each sputter cycle.

RESULTS AND DISCUSSION

In Figure 1a the microstructure and XPS survey spectra of basic substrates surface (Figure 1b) could be seen.

From the surface observation and obtained results it could be concluded that the surface of basic substrates was pure without any impurities (C, O, etc.). On this basis we concluded that the substrates were suitable for further experiments of Rh plating. The surface was slightly rough according to the previous mechanical treatment with a different tool on the industrial level.

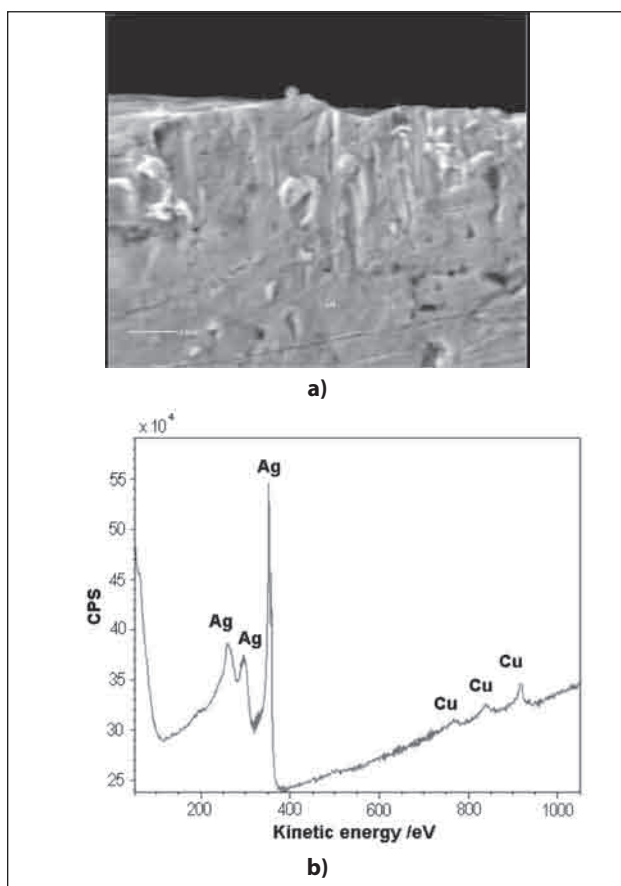


Figure 1 Auger micrograph (a) and XPS spectra of Ag 925 substrate (b)

During the performance of experimental Rh plating there were no problems. The Rh plating ran continuously. After plating the substrate was cleaned with alcohol and dried in hot air for 15 min. In Figure 2 the microstructure (Figure 2a) and XPS spectra of the substrate's surface (Figure 2b) which was Rh plated for 1 min could be observed. The determined thickness of Rh was about $0,3 \mu\text{m}$, which is visible as a red XPS spectrum. On the surface no other impurities were observed.

The second experiment was carried out under the same conditions, only the time was longer – 3 min. In Figure 3 the microstructure (Figure 3a) and XPS spectra of the substrate's surface (Figure 3b) which was Rh plated for 3 min can be seen.

In this experiment the formatted Rh layer is wider by about $0,2 \mu\text{m}$ in contrast to the previous test. Moreover, the Rh layer is very compact and serried. Such an Rh-layer could be applicable for different uses in jewels and other industries.

A further experiment was carried out with the aim of detecting the saturated position of Rh loading by plating on the surface of Ag 925 substrate. The time was prolonged to 5 min. From Figure 4 it can be seen that the thickness of the layer (Figure 4a) is the same as that from the experiment with 3 min. Also, the peak and position of the XPS spectra (Figure 4b) of the Rh layer

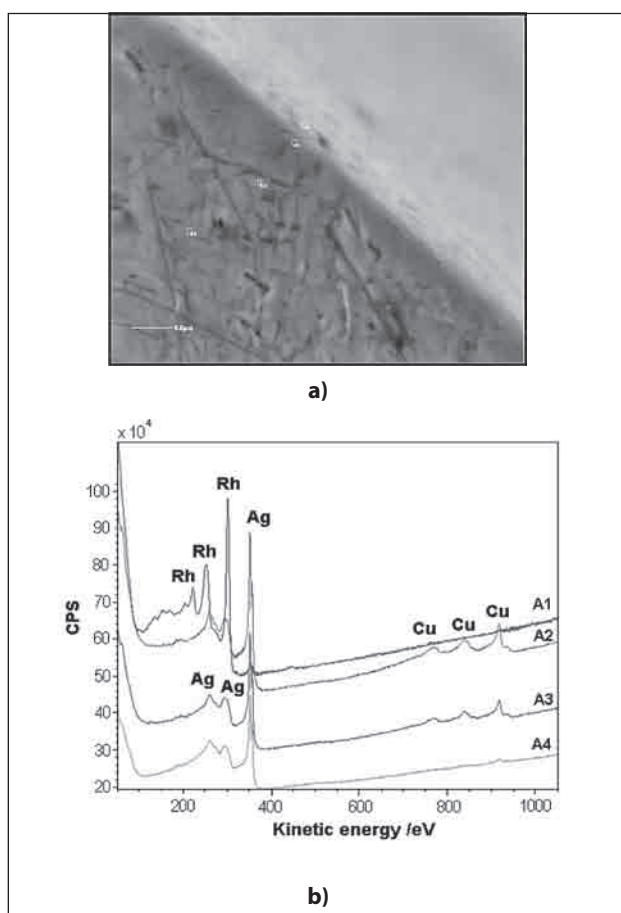


Figure 2 Auger micrograph (a) and XPS spectra of Ag 925 plate substrate surface (b) after Rh plating – 1 min

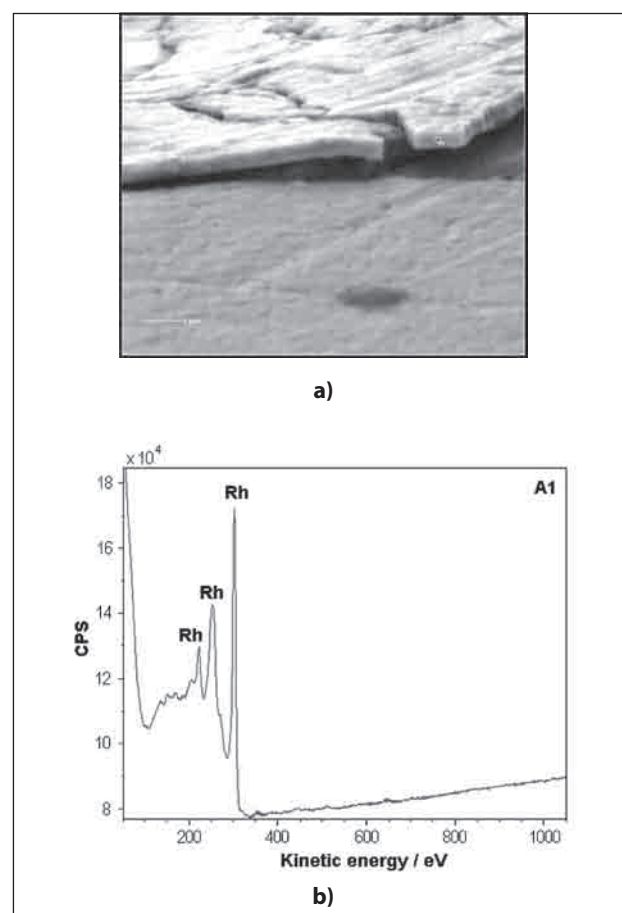


Figure 3 Auger micrograph (a) and XPS spectra of Ag 925 plate substrate surface (b) after Rh plating – 3 min

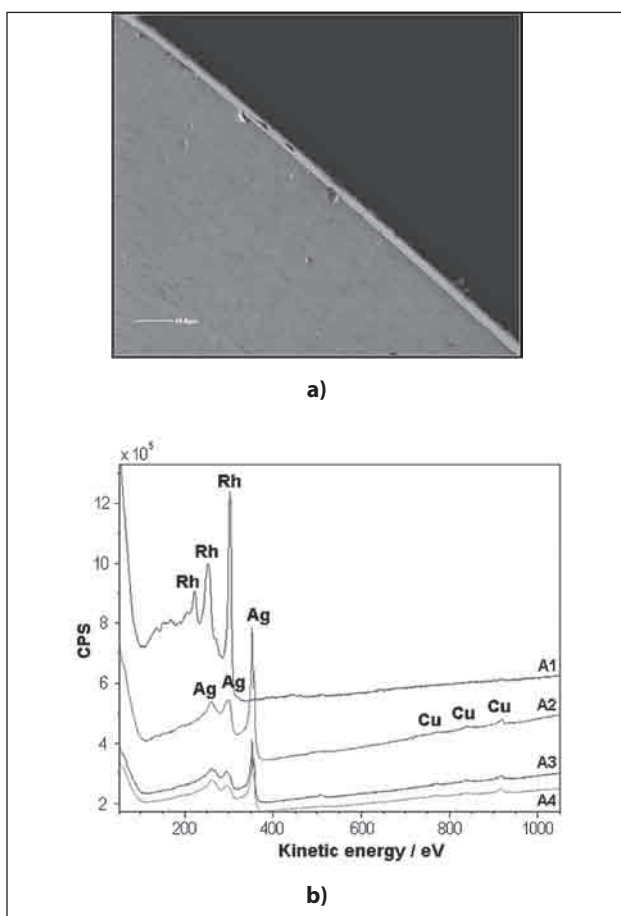


Figure 4 Auger micrograph (a) and XPS spectra of Ag 925 plate substrate surface (b) after Rh plating – 3 min

confirm a very stable structure and typical shape line for pure rhodium.

According to the above investigations we can conclude that the formatted layer of Rh on the Ag 925 substrate was qualitative and, on this basis, the technology was transferred into the industrial level in Zlatarna Celje d.d.

CONCLUSIONS

In this experiment the $\text{Rh}_2(\text{SO}_4)_3$ concentrate plus sulphuric acid was used. This rhodium electrolyte is the most used in Zlatarna Celje d.d.

Experiments showed that the formatted Rh layer over the Ag 925 substrate is of good quality. The optimal time of Rh plating is about 3 min, within which the

saturated Rh layer is formatted. The thickness of this Rh layer over Ag 925 is about 0,5 μm .

Acknowledgements

This article has been supported by the EUREKA Programme Cell-Ti E!5831 within the framework of the Ministry of Higher Education, Science and Technology of the Republic of Slovenia and Programme for Young Researcher within the framework of the Slovenian Research Agency. The authors thank Zlatarna Celje d.d., Slovenia, for working on the development of the new Ni-Ti alloy.

REFERENCES

- [1] E.R. Thews: *Metalloberfläche*, 10 (1956) 2, 85-89.
- [2] M.H. Smith: *Metal Finishing*, 41(1989) 1, 59-62.
- [3] M.L. Das: *Metal Finishing*, 46(1994) 1, 12-27.
- [4] P.A. Aeby: *Oberfläche-Surface*, 12 (1989) 1, 13 -15.
- [5] N. Contuzzi, S. L. Campanelli, A. D. Ludovico: *International Journal of Simulation Modelling*, 10 (2011) 3, 113-121.
- [6] M. Pleterski, T. Muhič, D. Klobčar, L. Kosec: *Metalurgija*, 51 (2012) 1, 13-16.
- [7] D. Williams: *Medical & Dental materials*, Oxford OX3, 1990.
- [8] A. Kushner: *Products Fin (USA)*, 67 (2002) 1, 20-22.
- [9] T.Y. Kometani, L.D. Blitzer: *Plating & Surface Finishing*, 15(1980) 1, 57 - 60.
- [10] F.H. Reid: *Metallurgical Reviews*, 8 (1963) 30, 167-211.
- [11] *Galvanotechnik*, 91 (2000) 4, 1004 - 1005.
- [12] K. Raić, R. Rudolf, P. Ternik, Z. Žunič, V. Lazić, D. Stamenković, T. Tanasković, I. Anžel: *Materials and Technology*, 45 (2011) 4, 335 - 339.
- [13] L. Gusel, R. Rudolf, B. Kosec, *Metalurgija*, 15 (2009) 1, 29-37.
- [14] I. Palčič, B. Buchmeister, A. Polajnar: *Journal of Mechanical Engineering*, 56 (2010) 12, 803-810.
- [15] K. Raić, R. Rudolf, B. Kosec, I. Anžel, V. Lazić, A. Todorović: *Materials and Technology*, 43 (2009) 1, 3-9.
- [16] I. Budak, B. Kosec, M. Soković: *Journal of Achievements in Materials and Manufacturing Engineering*, 54 (2012) 2, 233-241.
- [17] A. Stoić, F. Pušavec, J. Kopač: *Machining Science and Technology*, 13 (2009) 4, 516-528.
- [18] I. Budak, M. Soković, M. Barišič: *Measurement*, 44 (2011) 6, 1188-1200.

Note: The responsible translator for the English language is S. Hedges, Faculty of Mechanical Engineering, University of Maribor, Maribor, Slovenia