

Article

Electroplated Coatings for Magnetically Operated Contacts (Reed Switches)[†]

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Abstract: Electroplated coatings for reed switches were developed and investigated. The optimal compositions of industrial electrolytes currently used in the mass production of reed switches were given. The pros and cons of the different electroplated coatings, including those containing precious metals and with barrier layers of base metal alloys, were discussed.

Keywords: reed switches; electroplated coatings; precious metals; barrier layers

1. Introduction

Coating deposited on the working surface of the contact springs is a key structural element affecting the electrical conductivity and erosion resistance of the reed switches. At the present time, various deposition technics are used in reed switches production; however, the basic method is still galvanic plating (electrodeposition). Advantages of the plating, especially for quantity production, are simplicity of implementation and opportunity to fabricate multi-layered coatings of specified

composition and thickness. Electrodeposition is one of the most economic technologies, which is significant for the manufacturing cycles involving precious and high-cost metals.

The further progress in switchgear, the creation of the new types of reed switches have required developing appropriate coatings with specific structures and physical-mechanical properties. In practice, the formation of fine-crystalline, dense, and in some cases, bright deposits of the single metals determine the electrolyte composition and electrolysis mode. For alloys plating, the well controlled composition of the deposited coatings is also of great importance.

In this paper, we describe the development and production of different metals and alloys electrodeposited coatings currently used in the commercial manufacturing of reed switches.

2. Materials and Methods

For several years now, rhodium and ruthenium electrodeposited coatings with a gold underlayer and refractory metals (tungsten and molybdenum) coatings fabricated by vacuum deposition have been used worldwide for coatings in reed switch production [1-3].

Since the mid-seventies, Rh electrodeposition with gold underlayer has been successfully developed at our enterprise [4-6]. To produce the best quality Rh-coatings we used the electrolyte of the following composition (g.l⁻¹): rhodium (in terms of metal) of 4–12, sulfuric acid of 50–150 and sulfamic acid of 10–20. The deposition was carried out with the cathode current density of $(0.2 - 1) \times 10^{-2} \text{ A.cm}^{-2}$ at 40–50 °C.

Sulfate-sulfamate electrolyte has proved to be very stable under different operation conditions, with a useful lifetime of more than a year; it allowed fabricating high-quality coatings without cracks up to 5 µm of thickness. Rhodium is very appropriate material for the contact coatings of the reed switches for commutators and other electrical circuits with low current loads; its main drawback is a random increase of the intermediate (transient) electrical resistance at early stages of operation. It has long been known that Rh exhibits high catalytic activity stimulating surface adsorption of organic compounds that can result in the formation of organic polymer films onto the surface of the contact springs during switching. In order to prevent such negative process, the technological cycle of Rh-coatings production includes the redox (reduction-oxidation) annealing of the coated springs.

In the early nineties, the cost of Rh has considerably increased stimulating the search of cheaper contact materials which can substitute for rhodium in the coatings production without loss of the quality of reed switches. The only such material is ruthenium; it is cheaper and practically does not yield to rhodium in terms of the transient electrical resistance and physical-mechanical properties. Some physical and chemical properties of Ru and Rh are listed in Table 1.

As opposite to rhodium, there is no need to perform redox annealing of Ru-plated springs since during electrodeposition the protective oxide layer, preventing the formation of organic polymer films with dielectric properties, has been formed on the surface of ruthenium galvanic coatings. In spite of evident usefulness of Ru as a contact material for the reed switches production, at that period the ruthenium plating technology has been not elaborated. Our development of the industrial ruthenium plating technology of the reed switch contacts is described in [7-10].

Table 1. Comparison of some physical and chemical properties of ruthenium and rhodium.

<i>Physical and Chemical Properties</i>	<i>Ru</i>	<i>Rh</i>
Mass density (g.cm ⁻³)	12.2	12.4
Electrical conductivity at 0 °C ($\times 10^6$ S.m ⁻¹)	13.3	19.6
Thermal conductivity at RT (W.m ⁻¹ K ⁻¹)	109	87.8
Oxidation states	3, 4, 2, 6, 8	3, 2, 4
Pauling electronegativity	2.2	2.8

2.1. Ruthenium Plating

The Ru-deposition is carried out using the electrolyte of the following composition (g.l⁻¹): azanium μ -nitrido-bis[tetrachloroaquaruthenate (IV)] (in terms of metal) of 10–15, ammonium sulfate of 30–80; pH is less than 2. The deposition is carried out with the cathode current density of $(1 - 5) \times 10^{-2}$ A.cm⁻² at 65–70 °C.

The development of a stable ruthenium electrolyte for mass production is problematic due to its very complex chemical composition resulting in the complicated control of such electrolyte during the industrial plating. It relates to the ruthenium property (as opposed to rhodium) to be in electrolytes in eight different valence states and, as a consequence, to generate a great number of chemical complexes. The application of the binuclear nitrogenous-bridged anionic complex of ruthenium [Ru₂N(H₂O)₂Cl₈]³⁻ is the basis of our ruthenium plating technology. This complex is produced by the reaction of ruthenium (III) chloride with sulfamic acid [11]. The developed sulfamic electrolyte for ruthenium plating has been industrially produced for over 1–1.5 years.

2.2. Gold Underlayer Electrodeposition

The best electrolyte used for the fabrication of the gold layer between rhodium or ruthenium coatings and permalloy substrate is poor-porous gilding electrolyte with addition of thallium salt [12,13]. The typical composition of this electrolyte (g.l⁻¹) is: potassium dicyanoaurate (1) (in terms of metal) of 8–12, potassium phosphate dibasic trihydrate of 112–240, potassium dihydrogen phosphate of 28–60, tripotassium citrate monohydrate of 42–90, thallium (1) dihydrogen phosphate (in terms of metal) of 0.1–0.5; pH factor is generally in the range of 5.5–6.5. The deposition is carried out with the cathode current density of $(0.1 - 0.25) \times 10^{-2}$ A.cm⁻² at 50–60 °C.

Electrolyte of poor-porous gilding has a hybrid buffer including phosphates and citrates. In this case, thallium ions play a role of inorganic brightening additives slightly influencing on the gold microhardness. Gilding electrolytes used in the reed switches production are very stable; their lifetime is ca. 1.5–2 years. Prior gilding is obligatory before the main gold sublayer deposition; for that, citric-acid electrolyte of the following composition (g.l⁻¹) is used: potassium dicyanoaurate (in terms of metal) of 1–3, tripotassium citrate monohydrate of 100–185, 2-hydroxypropane-1,2,3-tricarboxylic acid of 100–185; pH is of 3.2–4.5. The deposition is carried out with the cathode current density of $(0.8 - 1) \times 10^{-2}$ A.cm⁻² at 50–60 °C.

The prior gilding improves gold adhesion with permalloy due to the formation of a great number of crystallization centers, especially, at the high current density. This electrolyte absorbs the permalloy impurities, which have been absorbed into the solution while the springs soaked in the electrolyte.

Until now, the ruthenium coating with gold sublayer has been the most commonly used coatings in the reed switches production. Depending on the reed switch design and application, the thicknesses of the gold and ruthenium layers can be varied. The functions of these layers are different: ruthenium coating inhibits erosion and gold sublayer provides a good adhesion of ruthenium with underlayers including permalloy substrate. The quality and thickness of the gold sublayer have an influence on the porosity and mechanical stress of the ruthenium coating. Also, the gold sublayer plays an important role as antidiffusion barrier under different thermal treatments (welding and annealing) of reed switches.

The failure cause analysis of the reed switches has shown that in the majority of cases increase of the transient electrical resistance, its instability and, finally, the erosion of the coatings occur when the components of permalloy (iron and nickel) and their compounds diffuse on the surface of the contact springs. The gold sublayer, even with the maximum thickness allowed by the reed switches design, cannot completely suppress this process. Considerably thicker gold layer is needed which is unreasonable from the technical and from the economical point of view.

For several years now, the method of Ru-coating electrodeposition with gold sublayer has shown itself to good advantage; however, not all technological problems have been completely solved. For example, it was found out that it is impossible to produce rather thick, more than 1 μm , ruthenium coatings without cracks. Moreover, it was ascertained that the mean time between failures for ruthenium-gold coatings depends on the working modes of reed switches, and in certain cases its number is far from optimal. However, the most essential disadvantage, which appeared in recent years, is the rise in prices of precious and rare metals that increases the self-cost of reed switches, making their production unprofitable.

2.3. Electrodeposition of Metal Alloys Coatings

At present, the primary task of the reed switches engineers is to find coating materials along with appropriate technologies, which can minimize gold and ruthenium consumption and keep, or even improve, the technical characteristics of the reed switches. Copper-nickel (20–40 wt.% of nickel), cobalt-tungsten (20–25 wt.% of tungsten) and nickel-molybdenum (20–25 wt.% of molybdenum) alloys are the most suitable materials, which are able to substitute for the precious and rare metals in the industrial reed switches production [14]. Due to their structural features, physical-mechanical and anticorrosive properties, these alloys can function as barrier layers. The microhardness ($\times 10 \text{ N}\cdot\text{mm}^{-2}$) of such galvanic coatings was found to be in the range of 200–400 for Cu–40 wt.% Ni, 200–280 for Co–20 wt.% W and 550–600 for Ni–20 wt.% Mo alloys.

For electrodeposition of the above-mentioned alloys we have developed the following electrolytes:

1. Pyrophosphate ammoniac electrolyte for copper-nickel coatings ($\text{g}\cdot\text{l}^{-1}$): copper (II) sulfate pentahydrate (in terms of metal) of 1.5–2.5, nickel (II) sulfate heptahydrate (in terms of metal) of 8–12, tetrapotassium pyrophosphate (general) of 180–220, potassium sodium tartrate of

20–30; pH is 8.5–9.5. The deposition is carried out with the cathode current density of $(1 - 2) \times 10^{-2} \text{ A.cm}^{-2}$ at 55–65 °C.

2. Tartrate ammoniac electrolyte for cobalt-tungsten coatings (g.l^{-1}): sodium tungstate dihydrate (in terms of metal) of 10–15, cobalt (II) chloride hexahydrate (in terms of metal) of 12–15, diazanium sulfate of 45–55, potassium sodium tartrate of 200–250; pH is 9–11. The deposition is carried out with the cathode current density of $(1 - 3) \times 10^{-2} \text{ A.cm}^{-2}$ at 50–70 °C.
3. Ammoniac citrate electrolyte for nickel-molybdenum coatings (g.l^{-1}): sodium molybdate (in terms of metal) of 3.0–4.5, nickel (II) sulfate (in terms of metal) of 4.5–5.5, nickel (II) chloride (in terms of metal) of 4.0–6.0, tripotassium citrate monohydrate of 55–100, azane of 60–80 (ml.l^{-1}); pH is 9.5–11.5. The deposition is carried out with the cathode current density of $(2.5 - 5) \times 10^{-2} \text{ A.cm}^{-2}$ at 30–45 °C.

Although these alloys exhibit good erosion resistance, they cannot be used as coatings for the reed switches on their own, because of the high value and instability of their transient electrical resistance. For that reason we proposed depositing the complex gold-nickel coating as a surface layer, containing up to 17 wt.% nickel, with a microhardness of 1600–2000 N.mm^{-2} . This coating, deposited even as a very thin layer (like lubricant) on the sublayer of the base metals or alloys with a high transient electrical resistance, reduces and stabilizes this resistance. The deposition is made using the electrolyte (g.l^{-1}): potassium dicyanoaurate (I) (in terms of metal) of 2.0–2.6, nickel (II) sulfate heptahydrate (in terms of metal) of 1.0–1.8, tetrapotassium pyrophosphate (general) (general) of 50–100, potassium sodium tartrate of 50–100; pH is 6.5–7.5. The deposition is carried out with the cathode current density of $(0.6 - 0.7) \times 10^{-2} \text{ A.cm}^{-2}$ at 30–35 °C.

Thus, each proposed coating *per se* cannot ensure the performance objectives. Only a combination of the layers, namely, the barrier layer of base metal alloys (Cu-Ni, Co-W, Ni-Mo) with complex Au-Ru or Au-Ni underlayer of a correctly selected thickness for each type of reed switch, allows attaining the required technical characteristics and economic effect, by saving the cost of precious metals. Test results for reed switches with the barrier layers of Cu-Ni, Co-W and Ni-Mo alloys, showed an increase of the mean time between failures; even twice as much for some operation modes.

3. Conclusions

Our developments of electroplated coatings used in magnetically operated contacts (reed switches) were summarized in this paper. We placed special emphasis on the economical technologies utilizing minimal amount of precious and high-priced metals without loss of the quality of reed switches. In summary, the improvement of plating technology and modification of reed switches constructions made it possible to:

- increase the range of switching loads;
- improve erosion resistance of reed switches;
- cheapen production prices of reed switches.

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