

Interaction of cobalt sulphide coatings with Pd(II) ions: cyclic voltammetry and XPS study

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During interaction of cobalt sulphide coatings with Pd(II) chloride solution cobalt in the coating is replaced by palladium and the replacement extent increases with the duration of reaction with Pd(II), the PdCl₂ solution concentration and temperature. Palladium in the modified coating exists mostly in the form of PdS; the presence of metallic Pd and mixed cobalt–palladium sulphide is probable. Under coating modification, the oxygen content greatly decreases and chloride is included into the sulphide layer. Cobalt sulphide coatings modified with Pd(II), unlike unmodified layers, can be directly electroplated by copper.

Key words: cobalt sulphide, palladium sulphide, cyclic voltammetry, XPS

INTRODUCTION

Copper sulphide coatings containing non-stoichiometric sulphide Cu_{2-x}S have been used in the last two decades as sublayers for direct electroplating of plastics. However, such metallization is reliable only when three cycles of Cu_{2-x}S formation are used [1].

The number of cycles of metal sulphide coating formation is reduced when cobalt sulphide is used instead of Cu_{2-x}S. Recently, the method of cobalt sulphide layer formation has been developed [2] and successfully applied for metalisation of plastics by nickel electroplating. However, before being electroplated with copper, cobalt sulphide coatings require modification.

One of such modification procedures is treatment of the cobalt sulphide coating with Ag(I) ions, when part of the coating components is replaced by ions of a more noble metal. As the reduction potential of silver sulphide is more positive compared with that of copper ion reduction from acid copper electrolyte, the modified coating on dielectrics is suitable for electroplating by copper [3].

A similar situation was expected for a cobalt sulphide coating treated with Pd(II) ions. This paper presents data obtained while investigating the interaction of cobalt sulphide layers with Pd(II) by cyclic voltammetry (CV) in KClO₄ solution and X-ray photoelectron spectroscopy (XPS).

EXPERIMENTAL

Formation and modification of cobalt sulphide coatings

Cobalt sulphide layers were formed by the method known as SILAR (Successive Ionic Layer Adsorption and Reaction method). In the first step, the substrate to be coated was treated for 30 s with a cobalt(II)–ammonia complex solution (the solution contained 0.16 M CoSO₄ · 7H₂O, 0.12 M (NH₂OH)₂ · H₂SO₄ and NH₃, pH ≈ 11; hydroxylamine was added to prevent cobalt(II) oxidation by air oxygen) at 20 °C and rinsed with water. During rinsing the Co(II) compounds adsorbed on the surface are hydrolyzed to insoluble compounds remaining on the substrate. At the second stage, the surface was treated with a sodium sulphide solution (1 M Na₂S) at 20 °C for 30 s and rinsed with water [4]. To obtain a thicker coating, the procedure was repeated. The cobalt sulphide coatings obtained were modified by treating with a freshly made palladium salt solution (0.3–2.26 mM PdCl₂ + HCl, pH = 2.2) at 20–40 °C.

Electrochemical measurements

The electrochemical behaviour of the coatings was studied by cyclic voltammetry (CV) in KClO₄ solution at a potential sweep rate 0.05 V · s⁻¹ using an Elchema potentiostat (USA) and Votscan data acquisition software. A standard electrochemical cell, a platinum net auxiliary electrode, an Ag/AgCl/KCl

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reference electrode with saturated KCl were used. The potential values are given with respect to SHE.

The working glassy carbon electrode (1.0 cm²) was prepared as follows. A glassy carbon (SU-1200) sheet (50 × 15 × 2 mm) was covered with polyvinyl chloride lacquer PVC-10 so that only an area of 1 cm² was left free, and then the Co sulphide coating was formed on the whole area of the sheet. Then the lacquer layer was removed and the same area was covered again with the same lacquer.

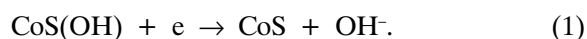
Characterization of the coatings

Co and Pd in the coatings were determined by atomic absorption spectroscopy using an AAS-603 spectrophotometer (Perkin-Elmer) after dissolving in aqua regia (HCl : HNO₃ = 3:1).

Both the cobalt sulphide coatings untreated with Pd(II) ions and the modified ones were analyzed by means of X-ray photoelectron spectroscopy (XPS). The spectra were recorded with an Escalab MK II spectrometer (VG Scientific, UK) using magnesium anode rays (MgKα – 1253.6 eV) with a 300 W power. The vacuum maintained in the cell of analysis was 1.33 · 10⁻⁶ Pa. To obtain the distribution of elements in depth, a gun of 1.0 keV Ar⁺ ion stream was used. Samples in the preparation cell were etched at a vacuum of 6 · 10⁻³ Pa and at a current of 20 μA/cm². These conditions correspond to an etching rate of ~5 nm/min. For XPS measurements, sulphide coatings were formed on 10 × 10 × 2 mm glassy carbon plates. XPS, photoelectronic spectra were recorded for the following elements: Co 2p_{3/2}, O 1s, S 2p, Pd 3d_{5/2}. The empiric factors of sensitivity for the elements were taken from literature [5], and the spectra obtained were compared with the standard ones [6]. The maximum accuracy of the method is ±0.1 at. %.

RESULTS AND DISCUSSION

Voltammograms recorded in KClO₄ solution for cobalt sulphide coating (formed by two cycles on glassy carbon electrode) at the negative-going potential scan from the stationary value to approx. -1.1 V show a large cathodic current peak K₁ in the potential region from -0.3 to -0.8 V (Fig. 1). This current most probably corresponds [7] to reduction of Co(III) to Co(II):



Both the CoS present in the coating and that formed in the reaction (1) are reduced to metallic cobalt at the potentials more negative than -1.0 V [7]:

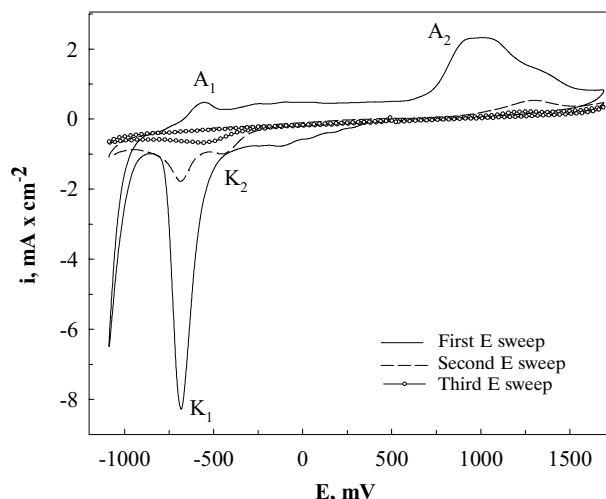
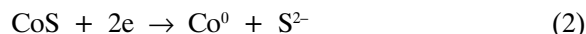


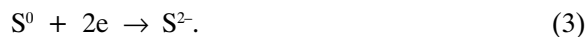
Fig. 1. Cyclic voltammograms recorded in 0.1 M KClO₄ solution for Co sulphide coatings formed on glassy carbon (GC) electrode in two cycles. In Figs. 1–4 the potential sweep rate $v = 50$ mV/s, $t^0 = 20$ °C



Simultaneously the evolution of hydrogen on the formed metallic Co takes place.

In the course of the subsequent anodic sweep, two anodic current peaks – A₁ (from -0.7 to -0.55 V) and A₂ (from 0.6 to 1.5 V) – are observed. In the potential region of peak A₁ an oxidation of metallic Co to Co(II) compounds – CoS and Co(OH)₂ – is supposed to take place, whereas peak A₂ is attributed to oxidation of Co(II) compounds to Co(III) and elemental sulfur [7].

At the second negative-going potential sweep, a sharp decrease of the current peak K₁ and an emergence of a small peak K₂ in the potential region from -0.3 to -0.55 V are observed. In this interval of potentials a reduction of the elemental sulphur formed at the anodic potential scan takes place:



At the second potential sweep in the anodic region, peaks A₁ and A₂ become almost undetectable. This indicates that in the course of the first cycle of potential scan most of electrochemically active species of the cobalt sulphide coating has been reduced and oxidized, some reaction products being removed from the electrode surface.

After treating Co sulphide coatings in PdCl₂ solution, the CVs change and these changes become larger while increasing the duration of the treatment.

For a sulphide coating treated with Pd(II) solution for 30 s (Fig. 2), the current peak K₁ shifts slightly to more negative potential values without

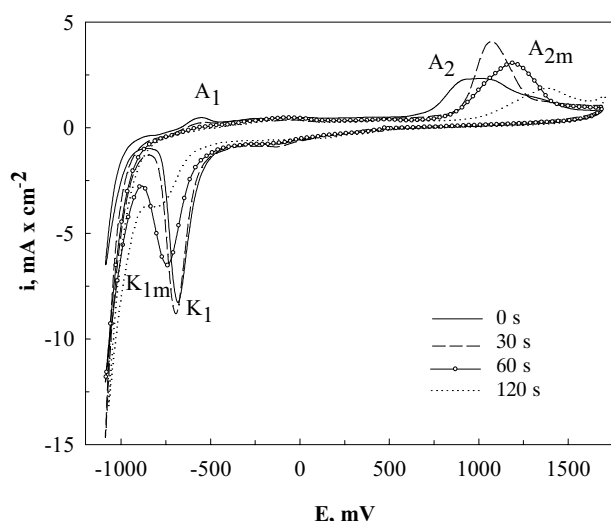
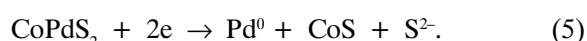
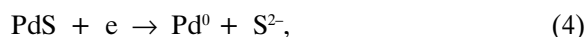


Fig. 2. Cyclic voltammograms recorded in 0.1 M KClO_4 solution for Co sulphide coatings formed on GC electrode in two cycles and treated with 0.56 mM $\text{PdCl}_2 + \text{HCl}$ (pH = 2.2) solution (at 20 °C) at a various duration of treatment

changing the form. After 60 s of treatment Cv becomes so different that it is possible to conclude that the peak K_1 related to the process of Co(III) reduction to Co(II) is replaced by the peak K_{1m} , of a lower height observed at more negative potentials; this peak can be attributed to the reduction of both the palladium sulphide and the mixed cobalt and palladium sulphide:



The probable reactions of the palladium sulphide species formation should include Co and Pd exchange:



The existence of such mixed sulphides has been described in [8, 9].

When increasing the duration of Pd(II) treatment, the peak K_{1m} diminishes and shifts to the more negative potentials, indicating a more difficult reduction of palladium compounds formed during interaction with cobalt species.

At the subsequent positive-going potential sweep, peak A_1 is eliminated and peak A_2 is transformed into peak A_{2m} at more positive potentials. With increasing the duration of Pd(II) treatment, peak A_{2m} shifts more and more to the anodic side (Fig. 2); it

can be related to palladium oxidation (standard potential of Pd/Pd^{2+} couple is 0.987 V) alongside with Co(II) oxidation to Co(III).

With increasing the temperature of PdCl_2 solution from 20 to 50 °C, changes observed in the CVs (Fig. 3) are similar to those found at increasing the duration of treatment.

Increasing the temperature from 20 to 30 °C, peak K_{1m} shifts to more negative potentials by ca. 0.05 V with a little change in the peak height; at the further rise of temperature to 50 °C, the peak K_{1m} height decreases but the peak potential remains practically the same (Fig. 3). A decrease in the peak height and a shift of the peak to more negative potential values obviously reflect a deeper interaction of the coating with palladium ions at a rising

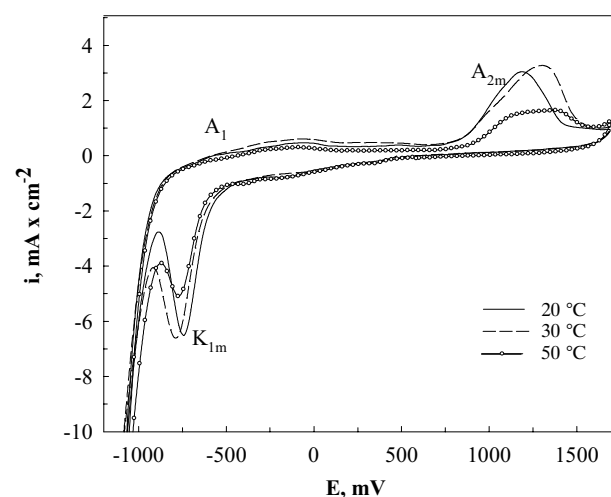


Fig. 3. Cyclic voltammograms recorded in 0.1 M KClO_4 solution for Co sulphide coatings formed on GC electrode in two cycles and treated with 0.56 mM PdCl_2 solution (duration of treatment 60 s) at different temperatures

temperature in a similar way as at increasing the of interaction time.

The subsequent potential sweep to the anodic region shows practically no peak A_1 and peak A_{2m} (in the potential region 0.95 ÷ 1.65 V). With increasing the temperature, peak A_{2m} diminishes and shifts to more positive potentials for the same reasons that have been analyzed when discussing the data in Fig. 2.

The form of voltammograms changes in dependence on PdCl_2 concentration in the solution used for cobalt sulphide modification (Fig. 4). At a palladium salt concentration 0.3–0.6 mM, the cathodic current peak K_{1m} is observed instead of peak K_1 characteristic of the unmodified cobalt sulphide layer. In the case of a higher PdCl_2 solution concentration (1.1–2.2 mM), in the cathodic region no current maximum is observed, but an appreciable catho-

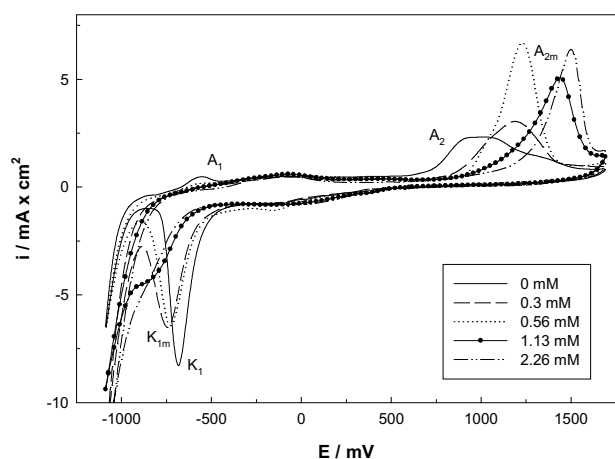


Fig. 4. Cyclic voltammograms recorded in 0.1 M KClO_4 solution for Co sulphide coatings formed on GC electrode in two cycles and treated with PdCl_2 solution of various concentrations. Treatment duration 60 s, $t^0 = 20^\circ\text{C}$

dic current appears before the hydrogen evolution region, in a potential range from -0.7 to -1.0 V. When sweeping the potential to more positive values, CV shows a peak A_{2m} which increases with increasing the concentration of PdCl_2 solution and, like in the cases discussed above, shifts more and more to the anodic region.

A conclusion can be drawn that the longer the duration of cobalt sulphide treatment with Pd(II) or the higher the PdCl_2 solution concentration or its temperature, the larger part of cobalt in the sulphide coating is replaced by palladium.

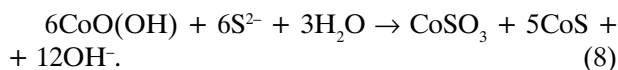
When studying the composition of cobalt sulphide coatings by XPS, the distribution of Co, S and O on the surface and in the depth of the unmodified coating was determined (Table). Cobalt and sulfur were the main components of the coatings, except for the surface; the largest amounts of cobalt

Table. Data of XPS analysis for Co sulphide coating before and after treatment with Pd(II)

| Conditions of etching | Element | Amounts, at. % | Bond energy, eV | Most probable composition of coating |
|---|---------|----------------|-----------------|--|
| Initial cobalt sulphide coating | | | | |
| Surface | Co | 16 | 778.7, 780.1, | CoS, sulphite, CoSOH Co(OH) ₂ |
| | O | 43 | 780.6 | |
| | S | 41 | 531.0, 533.3 | |
| 30 s – 20 μA (~1.0 nm) | Co | 33 | 778.1, 780.4 | CoS, sulphite, Co(OH) ₂ |
| | O | 22 | 531.0, 529.7 | |
| | S | 45 | 162.3, 167.0 | |
| 60 s – 20 μA (~2.0 nm) | Co | 41 | 778.0, 780.4 | CoS, sulphite, Co(OH) ₂ |
| | O | 18 | 531.0, 529.7 | |
| | S | 41 | 162.3 | |
| 120 s – 20 μA (~4.0 nm) | Co | 47 | 778.1, 780.4 | CoS, CoSOH |
| | O | 26 | 531.0, 529.7 | |
| | S | 27 | 162.3 | |
| 240 s – 20 μA (~8.0 nm) | Co | 44 | 778.1 | CoS, CoSOH |
| | O | 35 | 531.0, 529.7 | |
| | S | 21 | 162.3 | |
| Cobalt sulphide coating treated with PdCl_2 (0.56 mM, 30 $^\circ\text{C}$, t = 120 s) | | | | |
| Surface | Co | 4 | 778.8, 780.1 | CoS, sulphite, Co(OH) ₂ PdO, PdS, CoPdS ₂ |
| | Pd | 26 | 336.6 | |
| | S | 49 | 162.7, 166.3, | |
| | Cl | 21 | 164.4 199.1 | |
| 30 s – 20 μA (~1.0 nm) | Co | 6 | 778.1, 780.6 | PdCl ₂ CoS, Co(OH) ₂ PdO, PdS, PdCl ₂ CoPdS ₂ |
| | Pd | 40 | 335.7 | |
| | S | 45 | 162.7, 164.6 | |
| | Cl | 9 | 199.6 | |
| | Co | 8 | 778.1, 781.1 | |
| 60 s – 20 μA (~2.0 nm) | Pd | 44 | 335.6 | CoS, Co(OH) ₂ PdS, PdCl ₂ |
| | S | 40 | 164.3, 162.3 | |
| | Cl | 8 | 199.1, 199.9 | |
| | Co | 10 | 778.1, 781.6 | |
| | Pd | 52 | 336.6 | |
| 120 s – 20 μA (~4.0 nm) | S | 30 | 162.7 | CoS, Co(OH) ₂ PdO, PdS, PdCl ₂ |
| | Cl | 8 | 199.7 | |

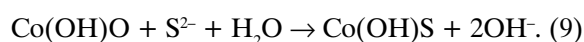
were found at a depth of 2–8 nm (over 40 at.%), and similar amounts of sulphur were determined only at the coating surface and at a depth of 1–2 nm, while in the deeper layers (4–8 nm) the amount of sulphur was much lower compared to that of cobalt. Cobalt sulphide layers are highly inhomogeneous, their composition changes largely with the distance from the surface. A large amount of oxygen, both on the coating surface (up to ~43 at.%) and in its bulk was found, indicating the presence of large amounts of oxides and/or salts in the coating.

XPS data showed the existence, alongside with cobalt sulphide CoS, of oxygen-containing compounds Co(OH)₂, CoS(OH) and sulphite on the surface as well as in the deeper layers. Co(OH)₂ apparently remained unreacted with sulphide ions in the second stage of the coating formation process, and sulfite was formed most likely in the secondary redox reaction according to the equation:



The content of CoSO₃ in the coating probably makes up only several percent of all the cobalt present in it and is formed near to the coating surface and should be reduced in the potential region of peak K₁.

Compound Co(OH)S can be formed in two ways: 1) by oxidation of Co(II) sulphide to Co(III) and subsequent hydrolysis to Co(OH)S; 2) by direct interaction of S²⁻ with Co(OH)O [10]:



After treatment with PdCl₂ this coating acquires quite a different composition: the content of cobalt and oxygen considerably decreases and the new components, palladium and chloride, appear.

Determination of oxygen in this system meets some difficulties. According to the published data [6, 11], in the presence of appreciable amounts of palladium (over 5 at.%) the palladium Pd3p_{3/2} XPS spectrum with a maximum corresponding to the bond energy value -531.9 eV overlaps with the oxygen O1s spectrum in the 525–550 eV interval, and the quantitative determination of oxygen becomes impossible. Palladium does not interfere in oxygen determination at lower levels (<5 at.%), when the effect of the Pd3p_{3/2} line on the O1s spectrum is negligible. The modified cobalt sulphide coatings contain large amounts of palladium, and therefore the exact quantity of oxygen remains unknown; by an approximate estimation, the oxygen content is at a several percent level. In Table, the oxygen content

is not given and the amounts of other elements were calculated neglecting oxygen.

The main metallic component of the cobalt sulphide coating treated with PdCl₂ solution, according to the XPS data (Table), is palladium. Its content in the coating's surface layer up to approx. 4 nm is ~85%, while the cobalt content is only ~15%. The metal composition determination by AAS, when all the coating had been dissolved, showed a slightly lower content of palladium (~80% Pd and ~20% Co). The difference can be explained by the understandable difficulties for Pd(II) ions in reaching the deeper layers of the coating and more of unreacted cobalt remaining there.

Palladium in the modified coating apparently exists mostly in the form of PdS both on the surface and in the depths. Mixed cobalt–palladium sulphide is present also in the coating surface layers. These results support our earlier conclusion about cobalt species transformation into palladium ones by reactions (6) and (7). Palladium probably exists also in a metallic state, especially when the total palladium content is over 50 at.%. The formation of large amounts of metallic palladium was found in a similar modification procedure of copper sulphide coatings [12], and the same palladium(II) reduction to metal by elemental sulphur can take place in the present case. Comparatively large amounts of chloride-containing species are found in the coating, especially on its surface; most likely chloride exists in the form of palladium chloride.

Cobalt remaining in the modified coating exists mostly in the form of sulphides CoS and CoPd₂; some amounts of oxygen-containing cobalt compounds as hydroxide and sulphite, remain also. The dramatic decrease in the content of oxygen-containing species under treatment with Pd(II) solution is caused not only by cobalt and palladium exchange but also by the action of HCl dissolving the cobalt oxo- and hydroxo-species.

When modified, the cobalt sulphide coating turns into the palladium sulphide one. This coating either contains a metallic component (Pd) or is considerably more easily formed at electrochemical reduction of palladium compounds compared to the initial cobalt sulphide coating. Apparently due to this difference dielectrics covered with coatings modified with Pd(II), in contrast to those covered with unmodified coatings, can be electroplated with copper from various copper-plating baths.

CONCLUSIONS

1. Under interaction of cobalt sulphide coatings with Pd(II) chloride solution, cobalt in the coating is replaced by palladium and the replacement extent inc-

reases with the duration of reaction with Pd(II), the PdCl₂ solution concentration and temperature.

2. Palladium in the modified coating exists mostly in the form of PdS; the presence of metallic Pd and mixed cobalt- palladium sulphide is probable.

3. In the modified coating, under the action of PdCl₂ and HCl the oxygen content greatly decreases and the chloride is included into the sulphide layer.

4. The cobalt sulphide layers modified with Pd(II), unlike the unmodified layers, can be directly electroplated with copper.

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KOBALTO SULFIDO DANGŲ SAŲEIKOS SU Pd(II) JONAIŠ TYRIMAS CIKLINĖS VOLTAMPEROMETRIJOS IR XPS METODAIS

S a n t r a u k a

Paveikus kobalto sulfido sluoksnius rūgščiu Pd(II) chlorido tirpalu, kobaltas yra pakeičiamas paladžiu; pakeitimo laipsnis didėja ilgėjant reakcijos su Pd(II) laikui, didėjant PdCl₂ tirpalo koncentracijai ir tirpalo temperatūrai. Didžioji paladžio dalis modifikuotoje dangoje yra sulfido PdS formos, jo dalis gali būti metalinio Pd ir mišrus kobalto-paladžio sulfido CoPdS₂ pavidalo. Modifikuotoje dangoje labai sumažėja deguonies ir atsiranda chlorido. Kadangi modifikuoti kobalto sulfido sluoksniai turi metalo (Pd) ir lengvai redukuojamų iki metalo paladžio junginių, jie geriau tinka naudoti kaip tarpinė laidi elektrai danga prieš elektrocheminį metalų nusodinimą ant dielektrikų paviršiaus, negu sunkiai redukuojama iki metalo pradinė kobalto sulfido danga. Paviršius su modifikuotu sulfido sluoksniu galima tiesiogiai elektrochemiškai variuoti iš įvairių elektrolitų.