Nanocrystalline cobalt-phosphorous alloy plating for replacement of hard chromium

Katarzyna Rymer, Andrzej Przywóski

ABSTRACT. Nanocrystalline cobalt-phosphorous (nCo-P) coatings electrodeposited by pulse plating are presented as a viable alternative to electrolytic hard chromium plating. An electrolytic process is evaluated for electrodepositing a cobalt alloy which contains at least about 2 to 25% atomic volume of phosphorous.
Electroplating of Co-P from citrate baths has been investigated under different conditions of current density and pulse sequences. The influence of these variables on the morphology, structure, hardness, internal stress and corrosion properties of deposited coatings has been studied in details.
Wide range of current densities can be applied in this electroplating process, but not greater than about 3,5 A/dm^2 to permit low stress plating. In general it is indicated that the hardness of Co-P deposits containing phosphorus concentrations between 3 to 25 wt%, can be increased to values exceeding 900VHN by annealing at a temperature greater than 300°C for a suitable period of time. Nanocrystalline cobalt-phosphorus (30 μm thick) exposed to the environment in a salt spray chamber operated according to the requirements of ASTM B117-97, performed very well, decreasing to only a 9/8 Protection/Appearance rating after 400 h exposure time.

INTRODUCTION

Chromium coatings are characterized by high hardness, low coefficient of friction, high corrosion resistance and high resistance to friction wear [1-2]. For these reasons, they have found many industrial application [3-4].
Cr (VI) compounds have clear carcinogenic effect, as well as strong caustic and oxidizing properties, which can contribute to emergence of ulcers and dissolution of the mucous membranes [5]. Cr (VI) compounds are also supposed to cause of the genetic modifications of human organism. These reasons mentioned above together constitute the answer to the question why nowadays we can observe the tendency to limit or exclude the application of Cr (VI) compounds from different branches of technology by the increasingly restrictive legislation. This is also the answer why there are conducted the extensive research on the application of alternative coatings with very good tribological and corrosion resistance properties. Scientists take into consideration as a replacement for technical chromium the usage of Ni-W, of Ni-P, of Co-P, of Co-W alloy coatings and coatings applied by HVOF technique[4, 6-7].

METHODOLOGY

Cobalt-phosphorus deposits were electroplated from the citrate baths containing: 80-100g/dm^3 citric acid, 100g/dm^3 cobalt(II) sulfate (VI), 30 g/dm^3 boric acid, 20g/dm^3 sodium hypophosphite and complex compound. The bath temperature was 333K. The pH of the plating bath was 3.5-4-0 adjusted by ammonia water or dilute sulfuric acid. The Co-P alloy electrodeposition was conducted using dc current and pulse plating methods. The electrolysis was carried out for 15-90 min, depending on the current density applied from the range of 1-5A/dm^2. In pulse deposition,

a PC computer was used to control the galvanostat. Two current waveforms were employed. Waveform 1 consisted of the reduction and rest pulses, T_{on} and T_{off}, of the same duration. In the waveform 2, T_{on} was two times bigger than T_{off}.
Specimens were soaked in the SECO/WARWICK vacuum furnace type 12.Ovpt-4035/36hv at 200-400°C for 1 hour, in the atmosphere of nitrogen.
Surface topography and composition of the deposits were examined using a scanning electron microscope LEO 435VP supplied with EDS analyzer.
Hardness of the deposits was determined with a Vickers method. The load used in the hardness measurements was 10g.
The variation of the internal stress with thickness during Co-P with citrate bath was determined using IS-dilatometer.
Alloys cobalt-phosphorus (30 μm thick) was exposed to the environment of a salt spray cabinet operated according to the requirements of ASTM B117-97 by 400h.

RESULTS AND SUMMARY

The results of influence of cathodic current density on the phosphorus content in the coating, in the studied range of parameters listed in Table 1 and illustrated graphically in Figure 1, allow to notice slightly lower content of phosphorus content in the coating with the increase of cathodic current density. The obtained concentration profile of phosphorus is beneficial from a technological point of view and allows the deposition of uniform coatings on objects with a complex surface geometry.

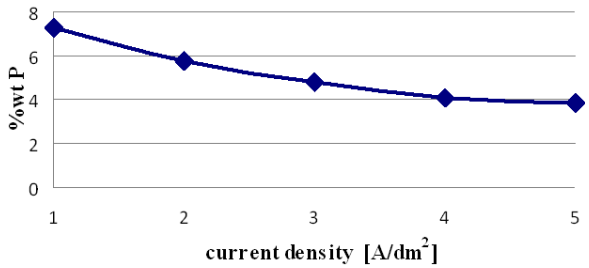


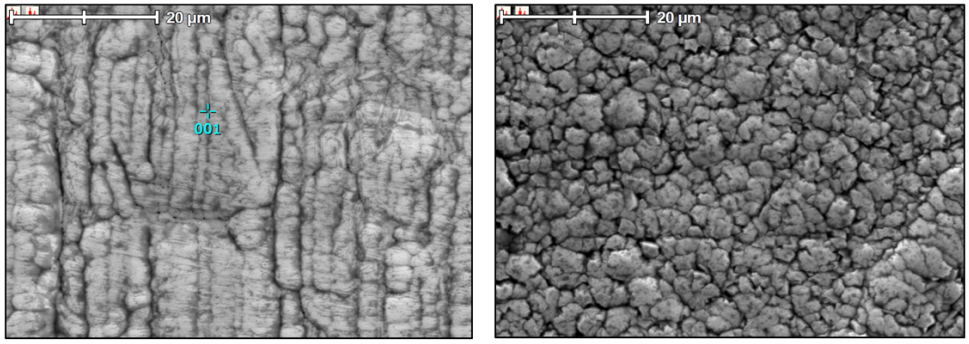
Figure 1: Influence of current density on contents of P in electrodeposited alloys.

Pulse current has a significant effect on P content in the coating. Changes in frequency of the current pulse causes smaller changes in phosphorus content in the coating, with a tendency to increase its content in comparison to the direct current deposition.

CURRENT DENSITY [A/DM²]		CONTENTS P IN ELECTRODEPOSITED ALLOY [% WT]
3	constant current	4.8
4.5	pulse current T_{on} = 2ms T_{off} = 1ms	5.23
4.5	pulse current T_{on} = 100ms T_{off} = 50ms	5.71

Table 1: Influence of deposited by pulse current methods on contents of P in electrodeposited alloys.

In investigated range of parameters, the embedded Co-P coatings were characterized by a high gloss, and with the phosphorus content greater than 3% wt. gloss finish was not deteriorating with increasing coating thickness. The use of pulse current in the examined range of parameters improved the smoothness of the coating, without affecting of its gloss.
The Co-P alloys had a different morphology. Depending on the applied cathodic current density which is related, among other things, with the differentiation of phosphorus content in the coating, At lower current densities surfaces of coatings were smoother and exhibited an amorphous structure. At higher current densities „cauliflower" structures were observed. In all cases, the coatings were coherent and didn't contain microcracks. The use of pulse current had a positive effect on the coating microstructure (Fig. 2). Pulse-deposited coatings revealed improved smoothness of the surface and reduction of the amount of coating defects, especially at the edges. Application of this type of alloy deposition made it possible to increase the amount of phosphorus in the coating by 20%.



(a) (b)

Figure 2: SEM images of surface of Co-P alloy deposited on copper (a) – pulse current method (waveform 1); deposition pulse time 10ms at current density of 6A/dm², rest pulse time 10ms at current density of 0 A/dm², (b) – constant current method, current density 3A/dm².

In the case of applying the Co-P alloyed coatings as replacements for technical chromium, the essential matter is their hardness. Obtained results presented that coatings without heat treatment, obtained by pulse current method, had a higher hardness (by about 100 HV) in comparison with coatings obtained by direct current method with the same process parameters. In all cases Co-P alloys showed lower hardness than chromium coatings, but higher than the Ni-W coatings, used as a replacement for the technical chromium.
Heat treated Co-P coatings at a temperature of 300°C, have revealed significant changes in hardness already after the half-hour of soaking. The hardness of coatings was doubled, after an hour of heat treatment, in comparison with the coatings tested immediately after their deposition. Co-P coatings applied by pulse current method with different frequencies and different relaxation times, just after the deposition, had similar hardness (and phosphorus content), while after heat treatment at the tested temperature and time of treatment, hardness of coating considerably varied (Table 2).

ELECTRODEPOSITED ALLOY	TIME OF HEAT TREATMENT [H]	HARDNESS HV 0,1	
		Temperature °C	
		without heat treatment	300
Co-P constant current	1	642	1309
Co-P pulse current T_{on} = 2 ms T_{off} = 1 ms	1	763	1451
Co-P pulse current T_{on} = 10 ms T_{off} = 10 ms	1	742	1224
Cr constant current	1	800-1050	700-1000
Ni-W constant current	1	450-550	720-900

Table 2: Influence of heat treatment on hardness Co-P, Ni-W, Cr alloys, thickness30 ±5µm

The use of pulsed currents for the deposition of the Co-P coatings caused the increase of stress values in comparsion to the coatings deposited by direct current method, however stresses still had compressive nature. During analysis of forming of the first 5 µm of alloy it was observed that residual stresses was lower for coatings deposited by pulse method (Fig.2). Above 10 µm coatings obtained by pulse method had lower values of compressive residual stresses (Fig.3). Use of different frequencies allowed to notice that the increase in frequency reduced the values of compressive stresses.
Nanocrystalline cobalt-phosphorus (30 µm thick) exposed to the environment of a salt spray chamber operated according to the requirements of ASTM B117-97, performed very well, decreasing to only a 9/8 Protection/Appearance rating after 400 h exposure time.
The technology of electrolytic deposition of Co-P coatings from developed solution enables the economical production of coatings with good protection values and high resistance to abrasive wear. Properties of coatings allow to use them as replacements for chromium coatings, especially in the automotive industry, or as an economic complement of the technology of electroless deposition of Ni-P coatings, particularly for parts with a regular surface and high thickness.

Co-P alloy coatings produced by the developed method have considerably better corrosion resistance in neutral salt spray and much higher hardness than Ni-P coatings, while paralleled with coatings with similar phosphorus content and thickness. Pulse currents method was found useful for deposition of Ni-P and Co-P coatings, especially when taking into account its positive effect on the protective properties of produced layers.

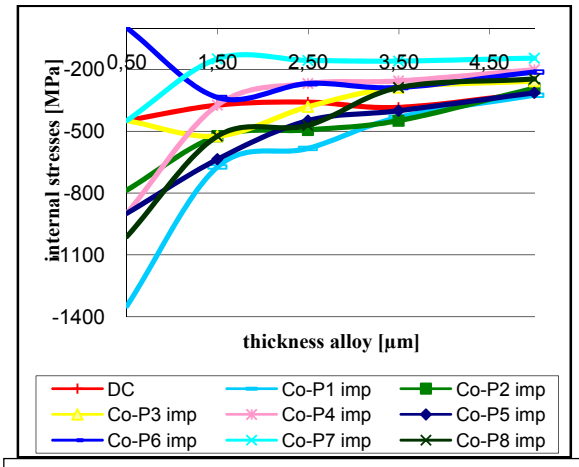
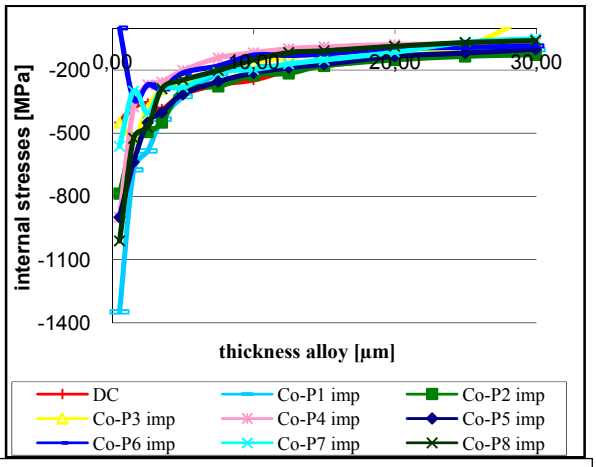


Figure 2: Influence of deposited by pulse current methods on internal stresses during deposited of the first 5 µm of alloy



AC: Co-P1 imp – T_{on}=1ms, T_{off}=1ms; Co-P2 imp – T_{on}=2ms, T_{off}=1ms; Co-P3 imp – T_{on}=10ms, T_{off}=10ms; Co-P4 imp – T_{on}=10ms, T_{off}=5ms; Co-P5 imp – T_{on}=100ms, T_{off}=100ms; Co-P6 imp – T_{on}=100ms, T_{off}=50ms; Co-P1 imp – T_{on}=500ms, T_{off}=500ms; Co-P8 imp – T_{on}=500ms, T_{off}=250ms

Figure 3: Influence of deposited by pulse current methods on internal stresses during deposited of 30 µm of alloy.

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