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Pulse Plating of Zn-Co Alloy Coatings

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Abstract: Pulse plating of Zn-Co alloys was studied using square pulse containing reverse current. The surface morphologies of Zn-Co alloy deposits were examined using scanning electron microscopy (SEM), and an attendant energy dispersive X-ray analyzer (EDA) was used to analyze the composition of Zn-Co alloy deposits. Results obtained showed that the average current density and reverse current density amongst all the variables investigated had very strong effects on the cobalt content and surface morphologies of Zn-Co alloy deposits. It is possible to electrodeposit Zn-Co alloy coatings with a very wide cobalt content range of 10-90 wt% by modulating pulse parameters.

Keywords: Electrodeposition**,** pulse plating, Zn-Co alloy.

Instead of being used as promising anti-corrosion coatings, electrodeposited Zn-Co alloys with controlled morphology and composition have also been the subject of many studies as a consequence of their observed catalytic activities[1-6]. However, most results reported on the electrodeposition of Zn-Co alloy coatings showed that the maximum amount of cobalt in Zn-Co alloys was about 6-7 wt%[7,8]. Zn-Co alloys with the cobalt content of more than 7 wt% have not been widely reported. This may be due to the perceived limitations arising from anomalous co-deposition according to the definition by Brenner[9].

Although pulse current (PC) plating technique was used to modulate the composition of zinc-based alloys by a few researchers[10,11], no work has been done on the electrodeposition of Zn-Co alloy using square pulse containing reverse current. In the present paper, investigations into the effects of pulse parameters on the pulse electrodeposition of Zn-Co alloy were carried out using a sulfate bath containing $ZnSO_4 \cdot 7H_2O$ 60 g/L, $CoSO_4 \cdot 7H_2O$ 140 g/L, $Na_2SO_4 \cdot 10H_2O$ 80 g/L, $(NH_4)_2SO_4$ 50 g/L, H_3BO_3 20 g/L, at PH=2-2.5 and a temperature range of 55-60 ℃. A computer-aided pulse plater unit (CAPP, Axel Akermenn A/S) was used during the electrodeposition of Zn-Co alloys. The basic waveform used is shown in **Figure 1**. Symbols marked in the schematic diagram, I_{p+}, I_{p-}, I_{av} and T, stand for positive peak current density (I_{p+}), reverse peak current density (I_{p-}), average current density (I_{av}) and cycle time (T), respectively. The frequency (f) of pulse is equal to $1/T$. During plating process, the value for reverse peak current densities (I_{p-}) was chosen to be a fraction of the positive

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Figure 1 A typical pulse waveform for the electrodeposition of Zn-Co alloys

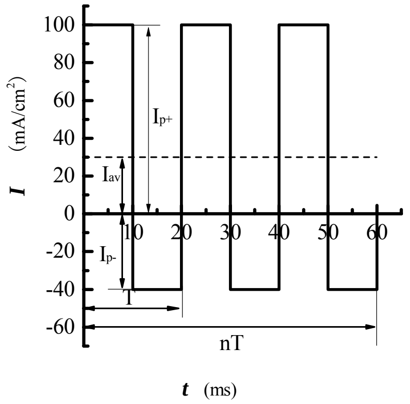
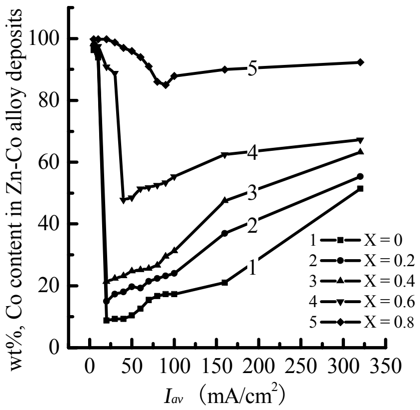


Figure 2 Effect of current density on the cobalt content in Zn-Co alloys



peak current density (I_{p+}), namely $I_{p-}= x{\cdot}I_{p+}$ (x = 0, 0.2, 0.4, 0.6 or 0.8). For a given average current density (I_{av}) and the value of fraction (x), the correlations between I_{av}, I_{p+}, I_{p-} and x are as follows:

$$I_{p+}=2I_{av}/(1-x) \qquad (1)$$

$$I_{p-}=x{\cdot}I_{p+} \qquad (2)$$

Among all the variables (I_{av}, I_{p+}, I_{p-}, x, T and f) presented above, only three of them are independent. I_{av}, x and f were chosen as the independent variables for the present study. **Figure 1** illustrates a typical pulse current waveform pattern based on the conditions of I_{av}=30 mA/cm^2, x=0.4, and f=50 Hz. The investigation on the effect of pulse parameters on the cobalt content in the Zn-Co alloy deposits was carried out by varying one parameter and keeping the others constant. The surface morphologies were examined using scanning electron microscopy (SEM) and an attendant energy dispersive X-ray analyzer (EDA) was used to analyze the composition of Zn-Co alloy deposits.

Figure 2 shows the variation of cobalt content in Zn-Co alloy deposits with average current density (I_{av}). It is evident that all the curves illustrate a similar profile. The cobalt content in the deposits is more than 90 wt%, if the average current density (I_{av}) is less than 10 mA/cm^2. But it decreases rapidly at the average current density of 20 mA/cm^2, then increases gradually with further increase in average current densities (I_{av}). The surface appearance of the deposits obtained at low current density was uniform but a little dull, whilst the deposits electrodeposited at average current densities higher than 20 mA/cm^2 were uniform and bright.

Figure 3 shows the variation of cobalt content with reverse fraction (x). The cobalt content in the deposits can also be modulated by varying reverse fraction (x) besides adjusting the average current density (I_{av}). Except for at low current density (less than 10 mA/cm^2), as shown by curves **1** and **2** in **Figure 3**, reverse current, amongst all the operating parameters investigated, has the greatest effect on the cobalt content in Zn-Co alloy deposits, when the average current density is more than 20 mA/cm^2. A significant variation of cobalt content in the Zn-Co alloy deposits was obtained by changing the reverse current (I_{p-}). For example, given an average current density (I_{av}), it

Figure 3 Effect of reverse fraction (***x***) on the Cobalt content in Zn-Co alloys

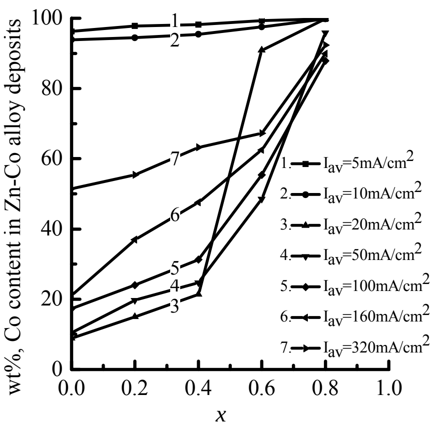
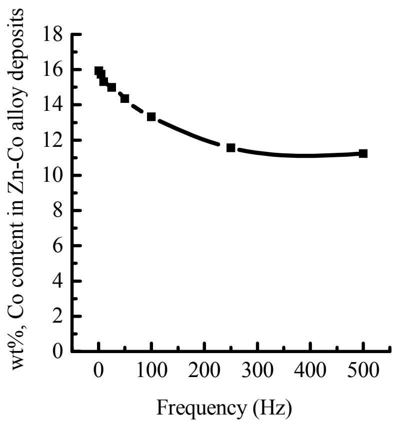


Figure 4 Effect of frequency (***f***) on the cobalt content in Zn-Co alloys*



* These data were obtained at the current density of 30 mA/cm^2 and fraction (***x***) of 0.2

is obvious that higher cobalt contents correspond to higher reverse fraction values (x). It is likely that the zinc component in the Zn-Co alloy deposit obtained during the cathodic part of the cycle dissolves selectively as the reverse current flows, resulting in an increase in the cobalt content of the deposit[12].

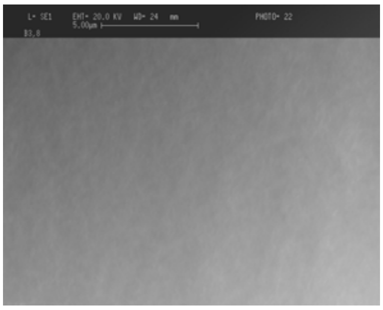
The effect of frequency on the cobalt content of Zn-Co alloy deposits was carried out in the frequency range of 1 – 500 Hz. **Figure 4** shows the variation of the cobalt content in Zn-Co deposits with frequency (f). It can be seen that the cobalt content decreased very slowly with increasing frequency. The cobalt content in Zn-Co alloy deposits remained relatively constant at about 12-16 wt% within the frequency range tested. However, micrographic examination showed that micro-cracks occurred at frequencies lower than 5 Hz, while micro-crack free Zn-Co alloy deposits were obtained, if the frequencies were more than 10 Hz.

Despite that the peak current densities (I_{p+} and I_{p-}) were not chosen as independent parameters, the effect of the peak current densities on the microstructural characteristics of the Zn-Co alloy deposits was also examined by adjusting the value of fraction (x) and keeping the other parameters constant. Micrographic examinations on the Zn-Co alloy deposits showed that an increase in peak current density resulted in considerable grain refinement. The reduction in grain size may be due to two causes. Firstly, the higher over-potential resulting from higher peak current density (I_{p+}) accompanied an increase in nucleation rate. Secondly, the big grains formed dissolves more quickly when the reverse current flows through [12].

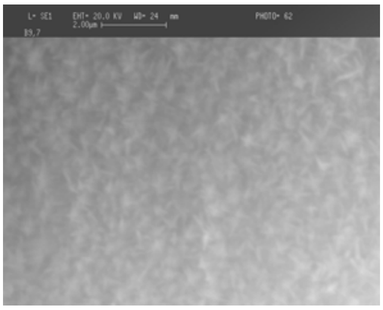
In summary, the results obtained from the investigation on the effect of pulse parameters on the cobalt content and surface morphology of Zn-Co alloys suggest that the cobalt content and the surface morphologies of Zn-Co alloys depend mainly on the average current density (I_{av}) and the value of the reverse fraction (x). Zn-Co alloy deposits with uniform, bright appearance and a wide cobalt content range of 10-90 wt% could be obtained by adjusting pulse waveform patterns only. **Figure 5** illustrates two

Zn-Co alloy samples with different surface morphologies and very wide range of cobalt contents obtained by modulating average current density (I_{av}) and reverse pulse fraction (x).

Figure 5 Surface morphologies of Zn-Co alloy deposits with a wide range of cobalt content



1 Co = 22 wt% (I_{av}= 70 mA/cm^2, x = 0.2)



2 Co = 94 wt% (I_{av}= 60 mA/cm^2, x = 0.8)

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