New Electrodeposited Rubber-bonding Alloy Coatings

Sergey S. Kruglikov. Valery I. Kharlamov and Tigran A. Vagramyan,
S.S. Kruglikov Consultants, Moscow, Russia

Conventional rubber-bonding brass coatings must have the proper composition and microroughness to ensure good adhesion of rubber to the basic metal surface. It is difficult to meet these requirements in cyanide-free solutions, especially for shaped parts with rough surface, where variations in local alloy composition and plate thickness may cause corrosion and adhesion loss. Codeposition of certain metals with copper-zinc alloy (e.g. nickel, cobalt or tin) considerably improves coating characteristics. The copper-to-zinc ratio becomes more stable because of more uniform macro- and microdistribution. The third alloying component also results in improved adhesion and corrosion resistance in microrecesses. Alkaline-tartrate type baths have been developed for the deposition of all the above-mentioned ternary alloys.

For more information contact:
Dr. Sergey S. Kruglikov
Bolshaya Spasskaya, 33-107
129090, Moscow, Russia
Phone – 7(095) 680-0281
Fax - 7(095) 200-4204
E-mail: mhasina@mail.ru

Introduction

One of industrial applications of brass electroplating is the special surface treatment for rubber-to-metal bonding [1]. Maximum adhesion is reached, if the coating contains 68±2% copper [2]. Another important factor is the microroughness of brass coating surface. Cyanide plating bath is considered as suitable for the deposition of brass coatings with required copper-to-zinc ratio.

Non-cyanide solutions e.g. pyrophosphate, tripolyphosphate and tartrate solution were also tested and some of them have been used in industry. However, comparative tests for the adhesion to rubber have demonstrated much better results for coating deposited from cyanide solutions. Since the adhesion depends on the composition of a brass coating any variations in the copper-to-zinc ratio over the cathode surface will produce negative effect on adhesion. Therefore brass plating solutions should be examined from the following positions:

1. Effect of current density on the composition of the coating.
2. Microdistribution of the deposit on the cathode surface.
3. Microdistribution of the components of the alloy.

If the composition of the alloy is changing depending on the current density, adhesion characteristics will be unstable especially on the shaped parts because of insufficient throwing power of the bath.

Depending on the type of the microdistribution of the alloy deposit the microgeometric characteristics of cathode surface may change in the course of the electrodeposition in opposite directions or stay practically unchanged. If a particular plating solution has high microthrowing power or is a leveling one, then the microroughness of the surface will gradually decrease in the course of the electrodeposition resulting in lower adhesion.

If a plating solution has poor microthrowing power (negative leveling), microroughness of the cathode surface will be gradually increasing and the adhesion will be improving.

In addition to the microdistribution of the alloy as a whole microdistribution of its components is a very important factor. If the alloy deposited on microprotrusions and microrecesses has different composition both adhesion and corrosion behavior may deteriorate, although the average composition of the alloy is close to optimum (68% Cu).

Major objectives of the present work were to study this problem in more detail and to develop a plating process capable to replace conventional cyanide brass plating bath for the deposition of rubber-to-metal bonding coatings.

Experimental Procedure

Following methods were used in the experimental study of the electrodeposition process and the alloy deposits obtained:

1. Measurements of current density and the overall deposition rate as the functions of the electrode potential and the composition of the solution.
2. Determination of average composition of the alloy deposited from the different solutions under potentiostatic conditions in stirred and unstirred solutions.
3. Microanalysis of the deposit in order to measure the variations in its composition and local thickness over the microprofile for different solutions and different values

of the cathode potential.

4. Measurements of the adhesion of rubber to the deposits for different time intervals between the plating and the bonding.

Following brass plating solutions have been used in the experiments:

1. Cyanide, Cu-Zn

CuCN 0.08 to 0.48 M
$Zn(CN)_2$ 0.075 M
NaCN (free) 0.17 M
pH 10.5
t 20 ^{0}C
E = -1.3 to – 1.7 V

2. Pyrophosphate, Cu-Zn

$CuSO_4$ 0.008 – 0.032 M
$ZnSO_4$ 0.21 M
$K_4P_2O_7$ 1.0 M
pH 8.0
t 20 to 55 ^{0}C
E = -1.03 to – 1.1 V

3. Tripolyphosphate, Cu-Zn

$CuSO_4$ 0.15 M
$ZnSO_4$ 0.22 M
$K_5P_3O_{10}$ 0.9 M
pH 7.0
t 20 ^{0}C
E = -1.05 to – 1.1 V

1. Tartrate, Cu-Zn

$CuSO_4$ 0.13 M
ZnO 0.03 M
$KNaC_4H_4O_6$ 0.94 M
NaOH 0,4 M
t 20 ^{0}C
E = -1.4 V

2. Tartrate, Cu-Zn-Co

$CuSO_4$ 0.13 M
ZnO 0.03 M
$CoSO_4$ 0.036 M
$KNaC_4H_4O_6$ 0.94 M
NaOH 0.4 M
t 20 ^{0}C
E = -1.4 V

Electrodeposition experiments were carried out under potentiostatic conditions. Polarization measurements were made using stationary, rotating disc and rotating cylinder electrodes. Microdistribution measurements were made using microsections of deposits obtained on microprofiled cathodes having a series of parallel ridges triangular in cross-section, 25±2 µm high and with approximately 100 µm distance between peaks. The average deposit thickness was measured gravimetrically. Local thickness was measured on microsections microscopically. Average deposits composition was determined by atom-absorbsion spectroscopy, and local one – by X-ray electron probe. Local current densities and local deposit composition were determined on selected areas, shown in Fig. 1, witch corresponded to micropeaks (Mp), microrecesses (Mr) and smooth (Sm) sites of surface. When calculating local partial current densities, initial surface area values were used and any changes in the surface area in the course of the electrodeposition were not taken into account.

Local partial current density, i_j, was calculated as follows:

$$i_j = \frac{\tilde{n} * S * N_j}{g_j * \ddot{A} * t}$$

were $\boldsymbol{\rho}$ is density of the deposited alloy, $\boldsymbol{S}$ is deposit cross-section area (found from microsections) on selected parts, $\Delta \boldsymbol{l}$, of the microprofile, $\boldsymbol{t}$ is duration of electrolysis, $\boldsymbol{N_j}$ is mass fraction of alloy component, and $\boldsymbol{g}_j$ is its electrochemical equivalent.

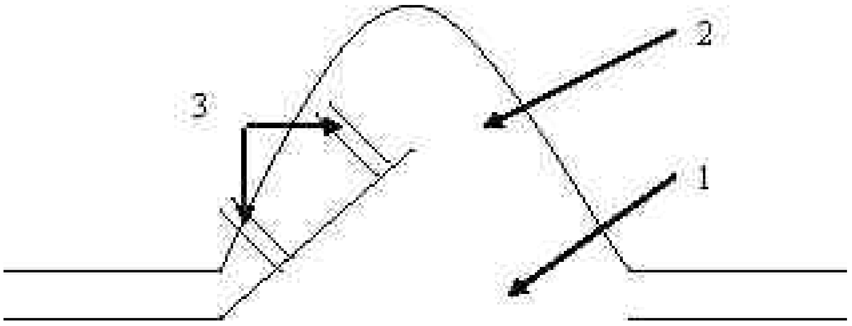

Fig.1 Measurements of local thickness' for calculations of partial current densities: 1-substrate (electroformed Ni plate); 2- deposited alloy; 3 – selected areas for thickness measurements.

Results and Discussion

All solutions studied are characterized by non-uniform distribution of the deposit thickness over the microprofile of the cathode surface (Figs. 2 to 6). The difference between local thickness on Mp and on Mr is especially high for all non-cyanide solutions. This means that the roughness of the surface will be gradually increasing in the course of the electrodeposition process. An increase in the true surface area resulting from growing microroughness may improve rubber-to-metal adhesion provided the chemical composition of the alloy is within optimum range.

However the analysis of the composition of deposits has revealed principal differences between the composition of Cu-Zn alloy deposited from non-cyanide solution on micropeaks, microrecesses and smooth areas of the microprofile (Figs. 3 to 5). Considerable deviations from the optimum values are probably responsible for poor adhesion of rubber to Cu-Zn coatings deposited from non-cyanide solutions. Moreover, adhesion was found to decrease progressively if time intervals between the electrodeposition of such coatings and the bonding operations are increasing.

Copper-zinc-cobalt alloy is the only coating with non-uniform microdistribution of deposit thickness and the composition of the alloy witch has shown better results than Cu-Zn coating deposited from cyanide solution (Fig. 7).

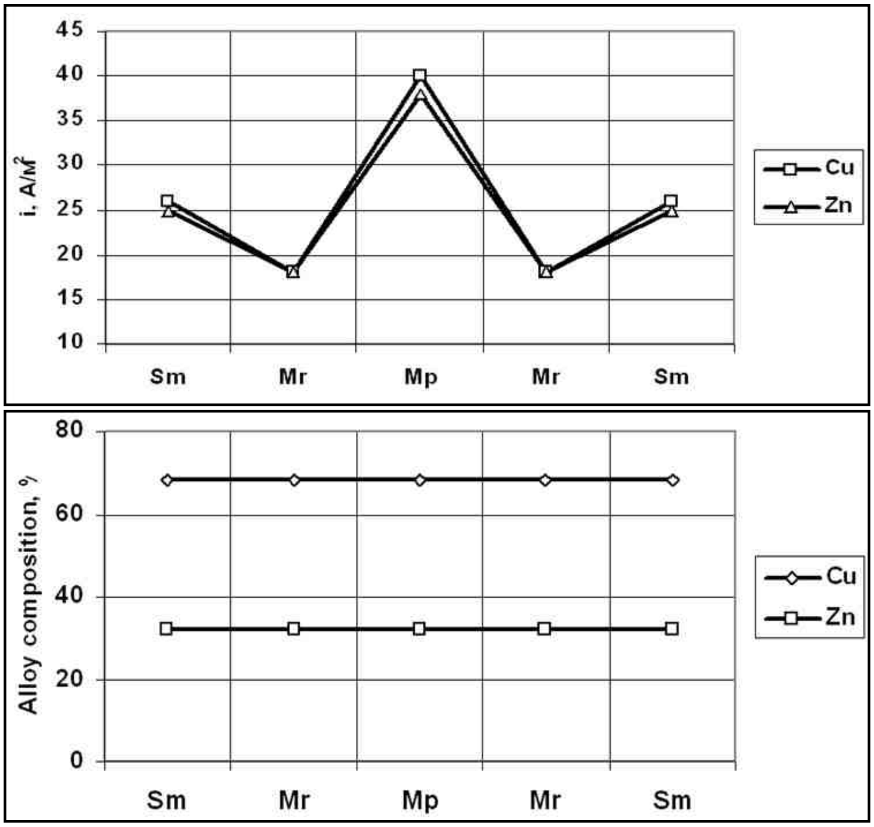

***Fig.2** Microdistribution of Cu-Zn alloy components and their partial current densities*
Cyanide plating bath: CuCN – 0.32 M; $Zn(CN)_2$ – 0.075 M; NaCN (free) – 0.17 M
pH 10.5; $t = 20^{o}C$; E = - 1.4 V

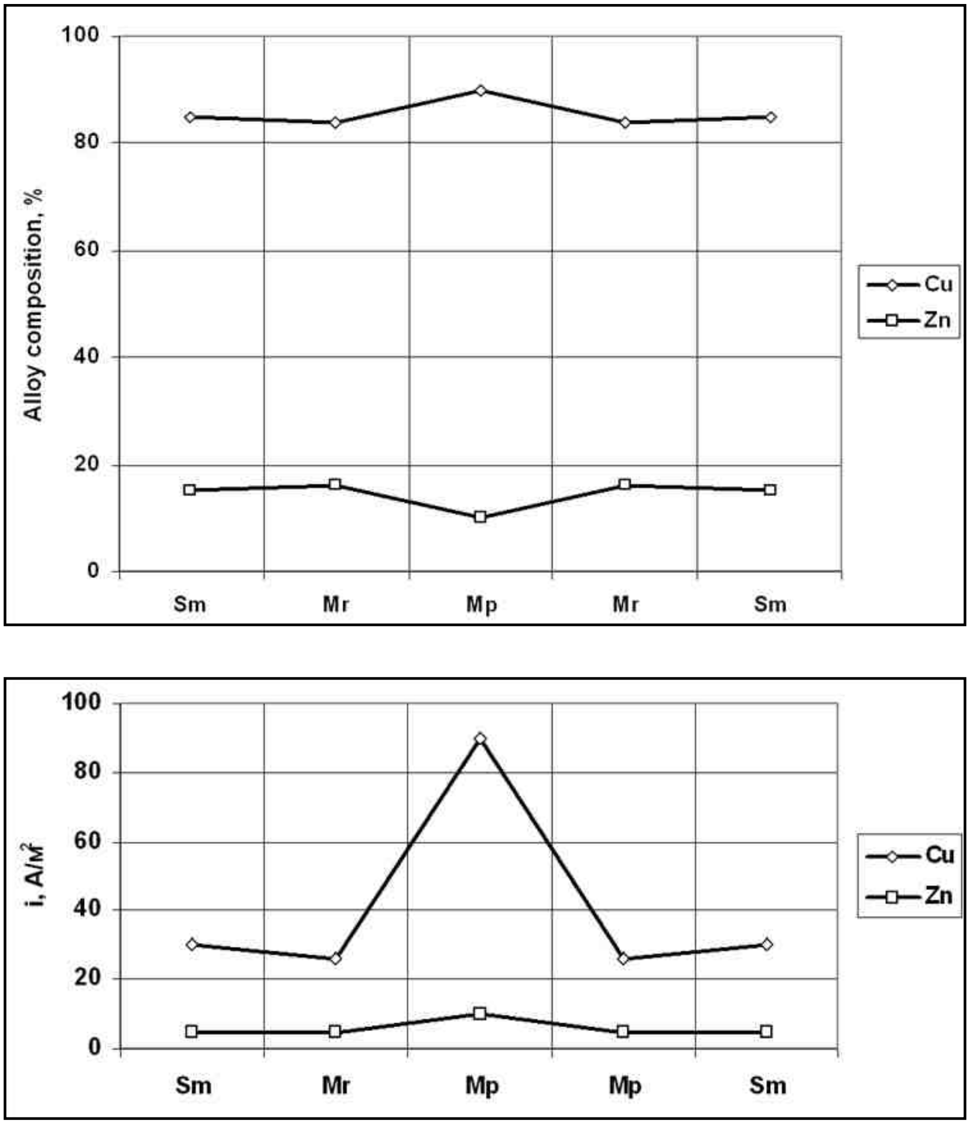

Fig.3. Microdistribution of Cu-Zn alloy components and their partial current densities
Tripolyphosphate bath: $CuSO_4$ *– 0.15 M;* $ZnSO_4$ *– 0.22 M;*
$K_5P_3O_{10}$ *– 0.9 M*
pH 7.0; t = 20 ^oC*, E = -1.1 V*

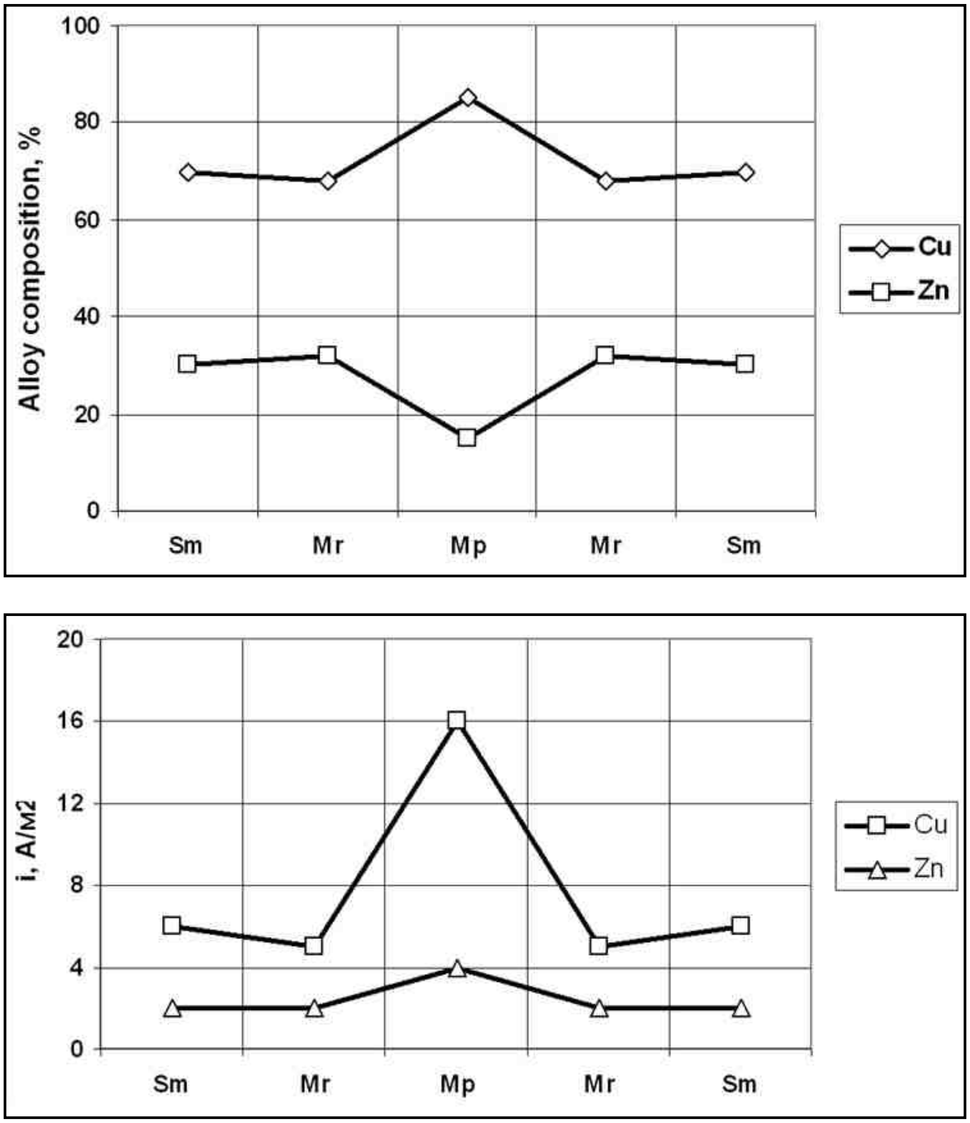

Fig.4. Microdistribution of Cu-Zn alloy components and their partial current densities Pyrophosphate bath: $CuSO_4$ – 0.008 M; $ZnSO_4$ – 0.21 M; $K_4P_2O_7$ – 1.0 M pH 8.0; t = 20 °C, E = -1.05 V

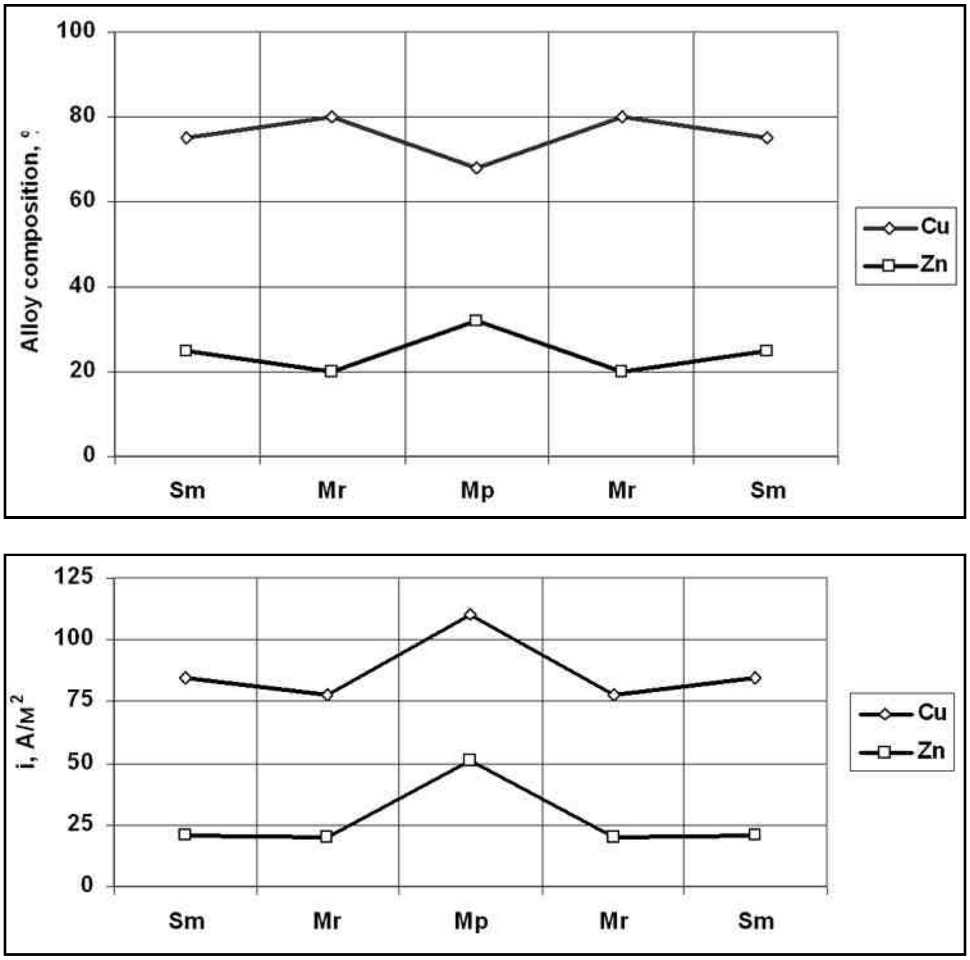

Fig.5. Microdistribution of Cu-Zn alloy components and their partial current densities
Tartrate bath: $CuSO_4$ *– 0.13 M; ZnO – 0.03 M;* $KNaC_4H_4O_6$ *– 0.94 M;*
NaOH – 0.4 M
t = 20°C; E = - 1.4 V

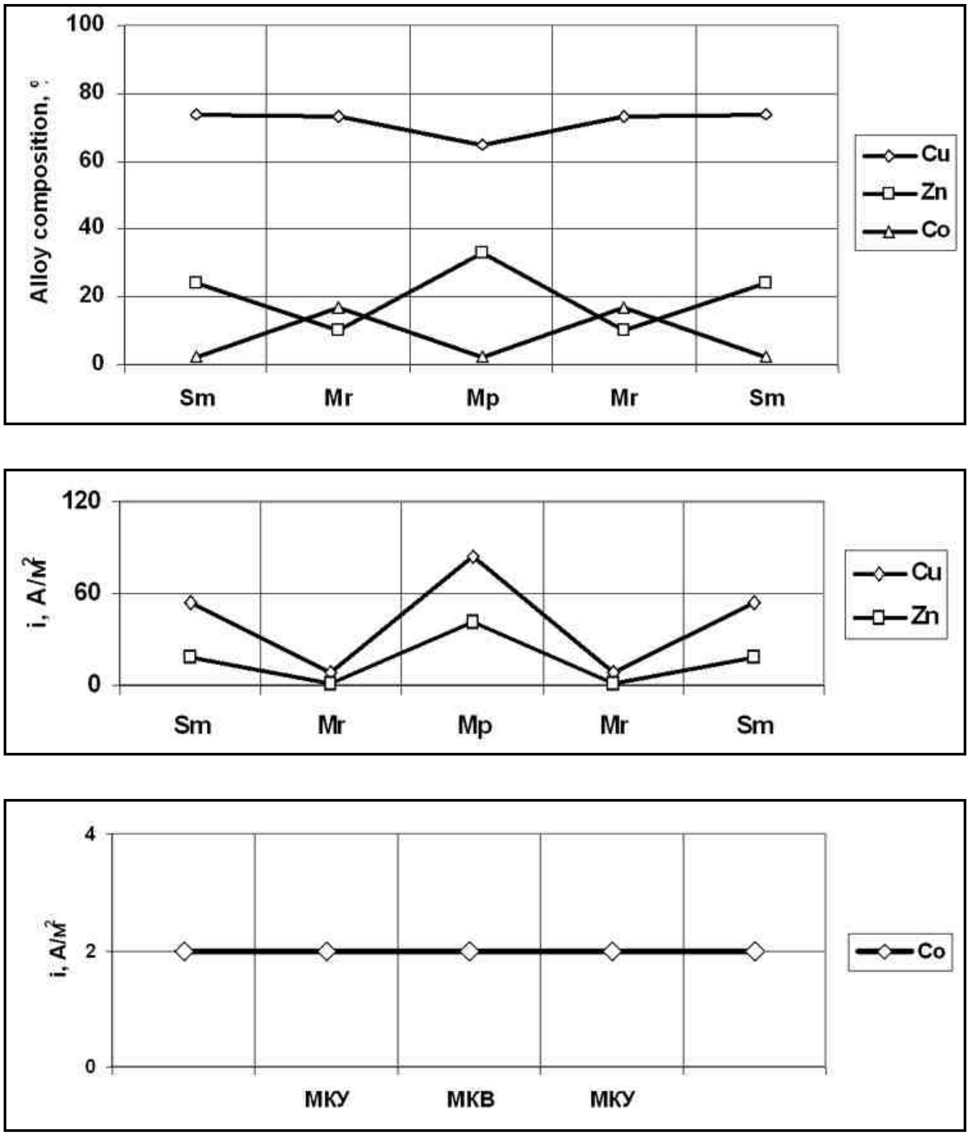

Fig.6. Microdistribution of Cu-Zn-Co alloy components and their partial current densities
Tartrate bath: $CuSO_4$ – 0.13 M; ZnO – 0.03 M; $KNaC_4H_4O_6$ – 0.94 M;
$CoSO_4$ – 0.036 M; NaOH – 0.4 M
t = 20°C; E = - 1.4 V

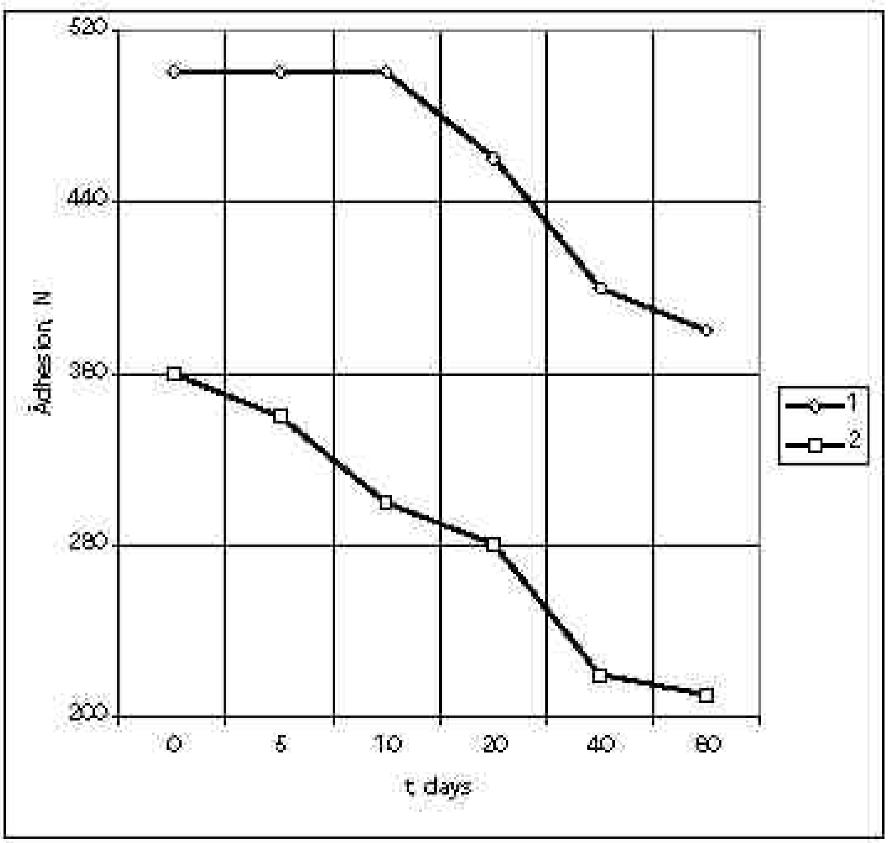

Fig 7. Rubber-to-metal bond strength:
1 – Cu-Zn-Co, tartrate bath: $CuSO_4$ – 0.13 M; ZnO – 0.03 M; $KNaC_4H_4O_6$ – 0.94 M; $CoSO_4$ – 0.036 M; NaOH – 0.4 M
2 – Cu-Zn, tartrate bath: $CuSO_4$ – 0.13 M; ZnO – 0.03 M; $KNaC_4H_4O_6$ – 0.94 M; NaOH - 0,4 M
Coating thickness - 5 µm; cathode current density - 4 A/dм^2

An important feature of Cu-Zn-Co deposits is quite uniform distribution of cobalt over the microprofile. This means that the concentration of cobalt in the alloy is lower at Mp and higher at Mr where the local thickness of the deposit is much smaller than at the peaks or at the smooth areas. In addition to high adhesion properties this alloy has much better stability than ordinary Cu-Zn coatings. Even after storage for 10 days before bonding it still has higher adhesion than as-plated Cu-Zn coating (Fig.7).

Conclusions

1. Only copper-zinc coatings deposited from cyanide bath have uniform composition over the microprofile.
2. The local composition of the coatings of similar average composition (68±2% Cu) deposited from non-cyanide plating solutions varies strongly over the microprofile. Therefore they are unsuitable for rubber-to-metal bonding.
3. Copper-zinc-cobalt coating deposited from tartrate solutions has better properties (high adhesion, longer storage time) than conventional Cu-Zn alloy deposited from cyanide solution.

References

1. S.S.Kruglikov, V.I. Kharlamov, T.A. Vagramyan, Proc./ AESF SUR/FIN 2002, p.648
2. Brenner A. Electrodeposition of Alloys. New York and London: Academic Press. – 1963. – Vol.1. – P. 714, P. 411-496