Elastic Copper- and Nickel-based Composite Coating

Sergey S. Kruglikov, Elena A. Tuzhilkina,
S.S. Kruglikov Consultans, Moscow, Russia.

Nickel- and copper-based composite coatings with relatively high content (30 vol %) of codeposited particles of thermoplastic resins can be converted into elastic layers suitable for high-pressure hermetically sealed couplings. The coating is produced by electrodeposition from a copper or nickel plating bath containing suspended particles of polytetrafluoroethelene, followed by thermal treatment at a temperature above its melting point. The polymer partially comes out of the coating creating a porous structure in the metal phase and polymer layer on its surface. Copper- and nickel-based coatings produced in this way have unusually low hardness, high elasticity and low friction coefficient, a combination of properties especially favorable for certain applications.

For more information, contact:
Prof. Sergei S. Kruglikov
Bolshaya Spaskaya, 33-107,
Moscow, 129090, Russia
Phone/Fax: +7-095-680-0281
Mob. phone: +7-916-616-9699
E-mail: mhasina@mail.ru

Introduction

Among functional electroplating processes the deposition of coatings for hermetically sealed couplings have good prospects for the application in the manufacture of devices which are used at elevated pressures or at high vacuum over wide temperature range. Such coatings have low friction coefficient, sufficient elasticity and strength. This combination of properties have been found in a new type of composite coatings. These coatings consist of metal phase, polymer phase and gas phase. The composite coating may include one or few metal phases as layers, dispersed organic polymer phase, dispersed gas phase (pores in metal layers) and a polymer phase as a top layer on the surface of the composite coating. A multilayer composite coating under investigation has been obtained by the electrodeposition of the following layers[1]:

1. Nickel layer;
2. Copper-polymer composite layer;
3. Nickel-polymer composite layer.

In the course of the subsequent thermal treatment some part of the polymer comes out of the composite layers and forms on the coating a top polymer layer. Total volume of pores formed in the composite coatings in the course of this post-treatment process is equal to the volume of the top polymer layer.

First nickel layer prevents contact deposition of copper from an acid solution.

Experimental Procedure

Individual layers of nickel or copper, composite layers and multilayer coatings were deposited on one side of stainless steel specimens 3,5×3; 4×6 and 9×2 cm. The other side was isolated. Plating cell had a magnetic stirrer. All plating processes were carried out at room temperature.

Three types of plating solutions were used:

1. High acid nickel bath

$NiCl_2 \cdot 6H_2O$	200 – 250 g/L
HCl (35%-ig solution)	180 – 200 g/L
c.d.	2 – 3 A/dm^2
deposition time	3 – 5 min

2. Sulphate copper bath

$CuSO_4 \cdot 5H_2O$	200 – 250 g/L
H_2SO_4	50 – 70 g/L
A_1	0.5 g/L
A_2	2.5 g/L
P	60 – 100 g/L
c.d.	1 A/dm^2

coating thickness	50 – 55 µm

3. Watts-type nickel bath

$NiSO_4 \cdot 7H_2O$	200 – 250 g/L
$NiCl_2 \cdot 6H_2O$	30 – 40 g/L
H_3BO_3	30 – 40 g/L
A_1	0.5 g/L
A_2	2.5 g/L
P	60 – 100 g/L
c.d.	1 A/dm^2
coating thickness	3 – 5 µm

P designates fine particles (av. size 2.5 to 3.0 µm) of copolymer of tetrafluoroethylene (~ 74%) and ethylene (m.p. 280 – 300 °C, decomposition temperature >350°C).

A_1 is an additive which stabilizes the suspension of microparticles. It has the following formula: $C_nH_{2n+1}O\ (C_2H_4O)_mH$, where n=14 to 16, m=20.

A_2 is a tetraalkyl ammonium salt – a cationic surface active additive.

After the electrodeposition process the specimens were rinsed in distilled water, dried at 60 – 80°C and subjected to thermal treatment at 280 – 300°C in the inert atmosphere for 1 hr.

Since the major part of the multilayer coating which determines its functional properties is the copper-polymer composite layer, some important characteristics of this layer have been studied in more detail. Distribution of included particles over the specimens surface and across the coating was determined. Total thickness and mass of the coating as well as its composition in mass and volume per cent were determined.

In order to evaluate possible deviations from average values a series of measurements was made on special long vertical specimens. These specimens with the coating were cut into 3 pieces which were examined separately.

Coating thickness was measured with a micrometer and also microscopically on microsections.

Mass of copper in the deposit was determined by stripping copper in nitric acid solution followed by the analysis of the solution obtained.

Results and Discussion

The properties of the polymer phase and its behaviaur during the stripping of the carting in nitric acid depenIf the plated specimen was not subjected to thermal treatment, the polymer particles passed into the nitric acid solution in a dispersed form and the stripping process took only few minutes. When the stripping was done after the thermal treatment a polymer film stayed on the surface of the specimen and the stripping process took many hours. A polymer film was formed on the surface of the coating during the thermal treatment due to partial transfer of liquid polymer from the pores in the metal matrix. This film has good protective properties and low friction coefficient. However a polymer film was observed after the stripping copper even on the specimens polished with emery paper after the thermal treatment. Stripping in this case took short time. This means that the polymer particles formed a separate porous structure in the course of thermal treatment followed by cooling.

Results of the measurements of the thickness and composition of copper-polymer deposite obtained under optimum conditions are given in Table 1.

Table 1. Thickness and Compositions of Copper-Polymer Composite Coating

Specimen №	Surface Area, cm	Current Density, A/ dm^2	Plating Time, hr	Average Thickness, μm	Coating Mass, g	Mass of Copper, g	Mass of Polimer, g	Volume Per Cent of Polimer
1	10.2	1	1	14.61	0.1036	0.0970	0.0066	30.05
2	10.9	1	1	17.86	0.1307	0.1210	0.0970	
3	23.0	1	1	17.19	0.2570	0.2354	0.0216	
4	10.2	1	2	29.59	0.2041	0.1894	0.0147	29.13
5	10.9	1	2	28.24	0.2103	0.1958	0.0145	
6	9.5	1	2	31.09	0.2000	0.1857	0.0143	
7	10.5	1	3	41.48	0.2949	0.2738	0.0211	29.82
8	10.5	1	3	47.04	0.3315	0.3069	0.0246	
9	10.5	1	3	43.6	0.3081	0.2855	0.0226	
10	23.4	0.5	1	7.48	0.1167	0.1078	0.0089	31.35
11	23.0	0.5	1	10.88	0.1678	0.1553	0.0125	
12	11.2	0.5	1	13.61	0.1010	0.0931	0.0079	
13	9.3	0.5	2	17.70	0.1096	0.1012	0.0084	30.80
14	8.4	0.5	2	18.11	0.1033	0.0960	0.0073	
15	23.0	0.5	2	23.10	0.3482	0.3198	0.0284	
16	10.5	0.5	3	26.95	0.1899	0.1758	0.0141	30.20
17	10.5	0.5	3	25.90	0.1810	0.1671	0.0139	
18	10.5	0.5	3	26.67	0.1895	0.1759	0.0136	
19	0.23	1.5	1	24.87	0.3742	0.3435	0.0307	30.78
20	8.7	1.5	1	25.33	0.1478	0.1368	0.0110	
21	10.4	1.5	1	23.85	0.1676	0.1555	0.0121	
22	10.2	1.5	2	36.35	0.2478	0.2291	0.0187	30.41
23	11.5	1.5	2	38.08	0.2931	0.2711	0.0220	
24	9.8	1.5	2	41.55	0.2732	0.2529	0.0203	
25	10.7	1.5	3	62.34	0.4517	0.4194	0.0323	29.77
26	8.7	1.5	3	64.48	0.3762	0.3482	0.0280	
27	10.4	1.5	3	58.08	0.4075	0.3779	0.0296	

They demonstrate high stability of the composition of the coating irrespectively of current density and coating thickness. This means high uniformity of the composition across the coating.

Data in Table 2 demonstrate the stability along the height of the specimen.

Table 2. Distribution of the Polymer Along the Specimen

Specimen №	Carrent Density, A/dm²	Platting Time, hr	Sections	Average Plate Thickness, μm	Volume Per Cent of Polimer
1	1	2	upper part middle lower part	31.74 32.04 37.35	28.00 28.00 26.57
2	1.5	1	upper part middle lower part	32.59 33.06 37.17	28.54 28.41 28.53
3	0.5	2	upper part middle lower part	17.38 17.27 19.27	30.16 31.20 30.88

An important property of the coatings studied is their microhardness. Some data on microhardness of nickel- and copper-polymer layers are shown in Figs. 1 and 2. It follows from these data that it is copper-polymer layer which is responsible for the properties of the multilayer coating determining their behaviour as a sealing coating. Pores in copper layer formed in the course at the thermal treatment and the transfer of liquid polymer to the surface of the coating create elasticity of the whole system and the top polymer film creates antifriction characteristics.

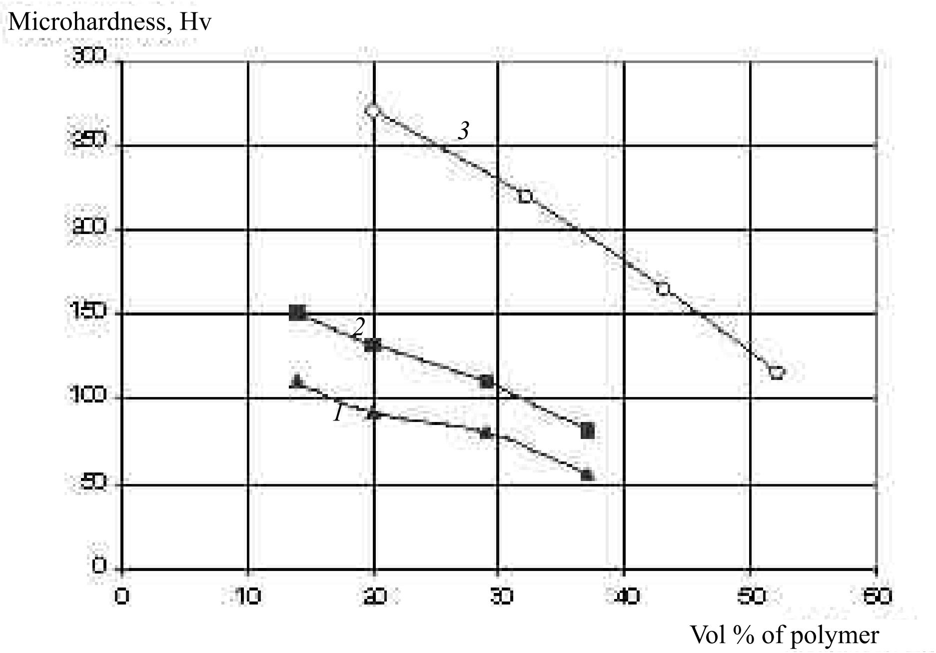

Fig 1. Microhardness of copper- and nickel polymer composite coating (50 μm). 1, copper, after thermal treatment; 2, copper, before thermal treatment; 3, nickel, after thermal treatment.

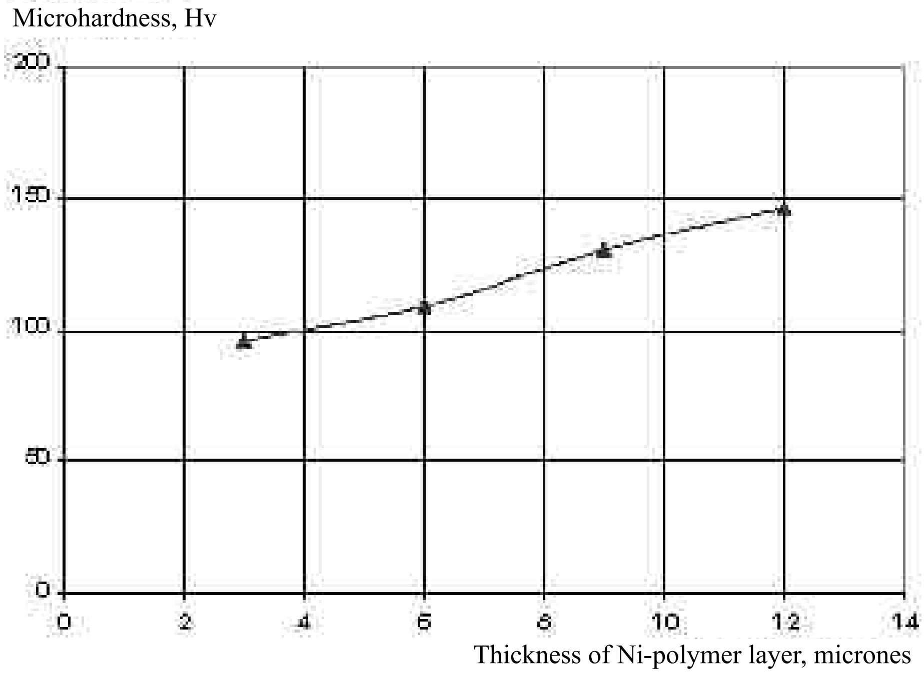

Fig 2. The effect of the thickness of top nickel-polymer layer (polymer content 42 vol.%) on microhardness of copper- nickel-polymer coating (copper-polymer 50 µm, polymer content 34 vol.%) after thermal treatment.

Conclusions

Copper-based composite coatings with relatively high content of chemically stable thermoplastic polymer can be converted into elastic antifriction coatings. These coatings may found various applications in different branches of industry.

References

1. L.K. Bobrovski et al. Report on Research Project 1987-1999. Yaroslavl State Technological University.