Research of Protective Properties of Microplasma Coatings

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Abstract – The results of the heat resistance research of MAO – coatings are presented. The coatings were formed in the electrolytes developed earlier. For an estimation of influence on heat resistance of the coatings in compounds of the transitive metals (Co, Cu), and also ZrO_2 were added into the electrolytes. It was found that at the temperature of 310 °C all the obtained coatings have strong coupling with the metal surface. An increase in the test temperature up to 500 °C showed that the silicate coating has the greatest heat resistance. It was shown that the participation of zirconium oxide at the formation of the coatings has an positive effect on its heat resistance.

1. Introduction

Development of the methods of the formation coatings capable to endure high temperatures remains topical task. Such coatings are applied in high-temperature catalysis, engine of internal combustion, etc. [1, 2]. Microarc oxidation is one of the modern methods which allows obtaining the coatings combining various properties [3, 4]. High temperatures and pressure in area of the microplasma discharge (a pressure about 600 At, a temperature – 2000–4000 °C) on the metal – electrolyte interface contribute to the formation of the coatings from electrolyte components and processable metal ions [5, 6].

The present work contains the experimental results connected to the formation of heat resistance coatings with compounds of transitive metals.

2. Experiment

Optimization of electrolyte compositions and processing modes was given in [7]. Stability of the formed coatings to thermocycle loading was investigated using a technique which was described in [8].

The coating composition was investigated by REM JSM-84 with the Link-860 adapter used for element analysis. The chemical composition of the surface layers of the samples was determined at three points located on the flat samples surface. The size of the analyzed area was 3.5 mm².

3. Result and Discussion

To estimate the heat resistance, the samples with the microplasma coatings (MAO-coatings) were tested for

thermocycle loads. Except for coatings formed in three base electrolytes, the coatings obtained in the electrolytes with the additive compounds of copper and cobalt, and also the ultradispersive powder (UDP) of zirconium oxide were used. The element composition of the coatings is submitted in Table 1. The results of the heat resistance tests are given in Table 2. First the samples were subjected to thermocycle loads at the temperature 310 °C for revealing the gradual mechanism of destruction, then they were tested at 500 °C before a complete destruction of the coating.

As it is seen from the data in Table 2, all the coatings except for No. 14 stood 250 cycles. On all samples the local infringements of the coating surface on the corners and sides (Fig. 1) were observed.



Fig. 1. The corner sides of the samples with a MAOcoatings. The right sample before thermocycles loads, the left sample after thermocycle loads

Estimating the total area of distractions, it is possible to determine change of the heat resistance of microplasma coatings depending on the additives in the base composition of an electrolyte.

The analysis of the data introduced in Table 2, showed that for the phosphate–citrate electrolyte the reduction of heat resistance was observed in the following direction of the sample number:

2 > 1 > 3 > 4 > 6 > 5

or phosphate – borate – fluoride electrolyte:

12 > 11 > 10 > 7 > 9 > 8.

It was shown that for the first electrolyte addition of copper and cobalt worsened the coating heat resistance. The exception was the coating which contained 2.5% of copper (Table 1). The minimum quantity of cobalt in coating (0.6% and 1%) also negatively influenced the heat resistance of the coating. The estimation of the influence of UDP on heat resistance of the coatings showed that though inclusions of ZrO_2 were not found in the composition of the coating, the formed coating had a higher heat resistance. Apparently, the presence of zirconium oxide renders influence on the formation mechanism of heat resistance coating.

Table 1. The element composition of coatings

Electrolyte composition. g/l	Supplementary components,	Element composition of coatings, mass. %							
, g.	g/l	Al	Р	Si	Fe	K	Zr	Со	Cu
$\begin{array}{rl} Na_{2}HPO_{4} \times 2H_{2}O &- & 40 \\ (C_{6}H_{5}O_{7})_{3}Fe \times nH_{2}O &- & 10 \\ (C_{2}H_{5}O)_{3}N &- & 25 \end{array}$	_	3.79	39.06	0.64	53.92	1.47	_	_	1.12
	$Cu(CH_3COOH)_2 \times 2H_2O - 3$	3.28	36.21	-	57.49	0.16	-	-	2.47
	$Cu(CH_3COOH)_2 \times 2H_2O - 5$	3.9	33.01	0.4	57.98	0.03	-	_	2.9
	$Co(CH_3COOH)_2 \times H_2O - 2$	3.42	34.43	0.26	58.42	0.68	-	1.56	0.56
	$Co(CH_3COOH)_2 \times H_2O - 4$	4.31	36.89	0.08	54.22	-	-	3.27	0.96
	$\frac{\text{Cu}(\text{CH}_3\text{COOH})_2 \times 2\text{H}_2\text{O} - 5}{\text{ZrO}_2 - 2}$	4.31	29.8	_	61.87	-	-	-	3.75
$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	-	20.92	44.81	1.01	0.81	6.55	-	_	7.98
	$Cu(CH_3COOH)_2 \times 2H_2O-2$	23.23	59.77	3.13	_	-	-	_	9.22
	$Cu(CH_3COOH)_2 \times 2H_2O-4$	17.73	63.95	0.31	0.42	1.76	-	_	14.12
	$Co(CH_3COOH)_2 \times H_2O - 2$	4.86	46.13	-	1.33	0.99	-	40.61	5.3
	$Co(CH_3COOH)_2 \times H_2O - 4$	5.14	38.79	0.2	2.16	0.67	-	48.11	4.43
	$ZrO_2 - 2$	10.83	74.08	0.83	1.42	1.77	-	-	4.31
$\begin{array}{cc} Na_2SiO_3-&200\\ KOH-&6 \end{array}$	_	-	-	64.01	1.96	32.1	_	-	1.24
	$ZrO_2 - 2$	-	_	65.53	1.02	31.77	2.1	-	1.68

Table 2. Research results of heat resistance of the MAO-coatings

Electrolyte composition, g/l	Supplementary components, g/l	Number of samples	Thermocycle quantity at temperature 310–15 °C	Thermocycle quantity at temperature 500–15 °C	
$\begin{array}{rl} Na_{2}HPO_{4}{\times}2H_{2}O-&40\\ (C_{6}H_{5}O_{7})_{3}Fe{\times}nH_{2}O-&10\\ (C_{2}H_{5}O)_{3}N-&25 \end{array}$	-	1	250	12	
	$Cu(CH_3COOH)_2 \times 2H_2O - 3$	2	250	19	
	$Cu(CH_3COOH)_2 \times 2H_2O - 5$	3	250	13	
	Co(CH ₃ COOH) ₂ ×H ₂ O – 2	4	250	13	
	Co(CH ₃ COOH) ₂ ×H ₂ O – 4	5	250	12	
	$\frac{Cu(CH_3COOH)_2 \times 2H_2O - 5}{ZrO_2 - 2}$	6	250	13	
$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	_	7	250	1	
	$Cu(CH_3COOH)_2 \times 2H_2O - 2$	8	250	1	
	$Cu(CH_3COOH)_2 \times 2H_2O - 4$	9	250	1	
	$Co(CH_3COOH)_2 \times H_2O - 2$	10	250	1	
	Co(CH ₃ COOH) ₂ ×H ₂ O – 4	11	250	1	
	$ZrO_2 - 2$	12	250	22	
Na ₂ SiO ₃ - 200 KOH - 6	_	13	250	21	
	$ZrO_2 - 2$	14	2	_	

In the case of the phosphate–borate–fluoride electrolyte, the situation is different. The coating obtained from an electrolyte with the additives of UDP (which were not found in composition of the coating) had the greatest heat resistance. Further there were coatings with the large contents of cobalt (40.6% and 48.1%). The copper additives (9.2% and 14.1% in the coating) had negatively effect on the stability under thermocycle loads.

On the surface of the silicate coating chipping was also observed on the sharp sides. The coating with small contents of zirconium collapsed after the second cycle. Obviously, it is connected to the inclusion of the UDP from the beginning of the coating formation and the difficulty of formation of the transitive gradient layer ensuring a strong coupling of the coating with a metal.

It should also be noted that the growth mechanism of local distructions was different various types of coatings. On the Al–P–Fe-coatings the distructions developed from corners on the sides, and on Al–Pcoatings it is more from the corners to the center and less on the sides.

The tests at 500 °C allowed comparing different kinds of the coatings. In all coatings from the phosphate–borate–fluoride electrolyte decreased heat resistance. It is explained by a smaller adhesion of the above coating [7], i.e. sharp transition from metal to oxide. The exception was sample No. 12, which stood 22 thermocycles at 500–15 °C. It is necessary to search for an explanation of the influence of the UDP in the electrolyte on the conditions of components delivery in the reaction area and on the electrical characteristics of the metal – solution interface [9, 10].

The silicate coating had the greatest heat resistance. Having poor hardness, such coatings due to the higher breakdown intensity have a strong bottom layer, consisting, mainly from α -Al₂O₃. Also, the large thickness of the coatings as compared to other coatings plays an important role here. Phosphate – citrate coating stood sustained 12–13 thermocycle at 500–15 °C. The small contents of copper in sample No. 2 resulted in an appreciable increase of heat resistance. This fact can also be explained by the influence of the additive on the structure of both the gradient and basic layer thickness, porosity, and density of coating.

It should also be noted that after destruction of the coating on all the samples there was a thin soft layer covering the metal surface.

Thus, the tests have shown that the additives of transitive metals and the UDP in some cases are capable of increasing considerably the resistance of microplasma coatings to heat resistance

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