Composite coatings of nickel-vanadium-phosphorus-nitride boron

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Abstract

The effect on the micro hardness of nickel-vanadium coatings from the concentration of sodium hypophosphite in the range 10-30 g/l, the concentration of boron nitride from 0 to 50 g/l, and from the temperature in the range of 50 - 90 °C was studied. The influence of these factors on the rate of coating, the appearance of the coating and the thickness of the coatings was researched. The effect of heat treatment regimes on the micro hardness of coatings when the composition, the temperature of the electrolyte and the heat treatment temperature change. The wear resistance of the obtained composite coating is determined. The composite coating of nickel-vanadium-phosphorus-boron nitride can be recommended for increasing the resistance of deforming tools operating at temperatures up to 600°C.

1. Introduction

In modern engineering, the problem of increasing the micro hardness and wear resistance of coatings applied to parts and tools is very relevant. For this purpose, galvanic chrome plating is mainly used. However, this process has a number of disadvantages, first of all, high toxicity of chromium electrolyte components, low scattering power, small current output, etc. Most often, for the replacement of galvanic chrome plating is using nickel-based composite electrochemical deposition processes are proposed, as well as chemical and galvanic nickel-phosphor coatings [1]. This work is devoted further development of these methods.

2. Materials and methods

Metal samples from carbon tool steel with a diameter of 20 mm and a height of 20 mm were used as the test samples. Before coating, samples were ground, polished, degreased with Viennese lime, decapitated in a 10% solution of sulfuric acid, washed with tap water and distilled water. The electrolyte was prepared from distilled water, chemically pure electrolytic materials and cubic boron nitride (elbor) were used. The grain size of the main fraction (95%) was 1 μm and smaller. The electrolyte was stirred with a propeller stirrer and thermostatic.

3. Investigation of the effect of the electrolyte composition and electrolysis regimes on microhardness and coating quality.

The object of the research were electrolytes for coatings, the basis of which was electrolyte No. 1 of the following composition: nickel sulphate 40 g/l, boric acid 20 g/l, vanadic acid 5 g/l, sodium nitritotriacetic acid 30 g/l. As the anode, a graphite electrode was used. The cathode current density is 1A/dm², the pH of the solution is 4.0. Sodium hypophosphite and cubic boron nitride were added to the basic composition of the electrolyte. The temperature of the electrolyte was varied according to the table 1. The influence of three factors on the micro hardness of coatings (Y) was studied: the concentration of sodium hypophosphite, the concentration of boron nitride and temperature. The upper
level for sodium hypophosphite $z_{1}^{\text{max}} = 30 \text{ g} / \text{l}$, lower $z_{1}^{\text{min}} = 10 \text{ g} / \text{l}$, $z_{0} = 20$, $\Delta z = 10$; the upper level for boron nitride $z_{2}^{\text{max}} = 50 \text{ g} / \text{l}$, the lower $z_{2}^{\text{min}} = 0 \text{ g} / \text{l}$, $z_{2}^{0} = 25$, $\Delta z = 25$; the upper level is temperature $z_{3}^{\text{max}} = 50 ^\circ \text{C}$, the lower $z_{3}^{\text{max}} = 90 ^\circ \text{C}$, $z_{3}^{0} = 70$, and $\Delta z = 20$. The planning matrix of experiment and the microhardness measurements in kg / mm$^2$ (yield $Y$) are shown in Table 1.

| №  | $z_{1}$ | $z_{2}$ | $z_{3}$ | $x_{1}$ | $x_{2}$ | $x_{3}$ | Yield Microhardness kg / mm$^2$ |
|----|--------|--------|--------|--------|--------|--------|---------------------------------|
| 1  | 10     | 0      | 50     | –1     | –1     | –1     | 350                             |
| 2  | 30     | 0      | 50     | +1     | –1     | –1     | 322                             |
| 3  | 10     | 50     | 50     | –1     | +1     | –1     | 446                             |
| 4  | 30     | 50     | 50     | +1     | +1     | –1     | 464                             |
| 5  | 10     | 0      | 90     | –1     | –1     | +1     | 792                             |
| 6  | 30     | 0      | 90     | +1     | –1     | +1     | 724                             |
| 7  | 10     | 50     | 90     | –1     | +1     | +1     | 824                             |
| 8  | 30     | 50     | 90     | +1     | +1     | +1     | 946                             |

The yield (micro hardness) was approximated by the linear equation

$$Y = b_{0} + b_{1}x_{1} + b_{2}x_{2} + b_{3}x_{3}$$ (1)

The coefficients $b_{i}$ were determined by the formula

$$b_{i} = \frac{1}{N} \sum_{j=1}^{N} x_{j i} y_{j}$$ (2)

Using the results presented in Table 1, the regression equation is obtained in the form

$$Y = 608.5 + 5.5x_{1} + 61.5x_{2} + 213x_{3}$$ (3)

It follows from Equation 3 that all three factors increase the micro hardness, while the micro hardness increases the most with increasing temperature of the electrolyte. This is due to an increase in the phosphorus content in the coating. Increases the hardness of the coatings and increases the concentration of boron nitride in the electrolyte, as this leads to an increase in the content of this very solid compound in the coating. The concentration of sodium hypophosphite is least affected by the micro hardness of the coatings.

The results of the effect of heat treatment on the micro hardness are presented in Table 2. From the results obtained, the regression equation was obtained to determine the microhardness of the coatings after heat treatment at $400 ^\circ \text{C}$ in the form

$$Y = 751.25 + 33x_{1} + 46.5x_{2} + 212.5x_{3}$$ (4)

Table 2. Planning matrix and micro hardness measurement in kg / mm$^2$ after heat treatment
Thermal treatment of coatings at 400 °C increases the micro hardness of coatings due to the formation of nickel and vanadium phosphides.

During the second heat treatment, the temperature of the furnace was increased to 600 °C, and the holding time was 1.5 hours. From the obtained results of micro hardness measurements (Table 2), it follows that there is a further increase in the micro hardness of the coatings of the samples, but a decrease in micro hardness in experiments Nos. 3, 4 and 7 is also observed. This seems to be due to the strengthening effect due to an increase in the concentration nickel and vanadium phosphides and with the softening effect of boron nitride arising at high temperatures.

The regression equation for this regime has the form

\[ Y = 812.75 + 121x_1 - 174.25x_2 + 150.23x_3 \]  

(5)

Further heat treatment at a higher temperature of 800 °C led to softening of the coating. Table 3 shows the results of the effect of the concentration of sodium hyposite (Z1), the concentration of boron nitride (Z2) and the temperature of the electrolyte (Z3) on the current efficiency, the coating rate, the appearance of the coating and the thickness of the coatings. Coating time in all experiments is 1 hour.

Table 3 Influence of the main factors on the current output, speed and type of coating

| Temperature and additives introduced into the electrolyte-base No. 1. | Current yield % | Speed of application, μm/min | The thickness of the coating μm | Appearance of the coating |
|---|---|---|---|---|
| Z1=10, Z2=50, Z3=50 | 84.35 | 0.184 | 11.041 | Gray, frosted |
| Z1=30, Z2=50, Z3=50 | 73.37 | 0.160 | 9.603 | Semi-shiny |
| Z1=30, Z2=0, Z3=90 | 104.32 | 0.227 | 13.633 | Shiny |
| Z1=10, Z2=50, Z3=90 | 110.48 | 0.241 | 14.461 | Light gray, frosted |
| Z1=30, Z2=50, Z3=90 | 108.41 | 0.236 | 14.189 | Semi-shiny |

Several processes often take place on electrodes during electrolysis, they are divided into basic processes (in our case this is primarily the separation of nickel and vanadium by electrolysis) and by-products (hydrogen evolution). The current yield was determined by the formula...
\[ CY = \frac{m(pr)}{m(th)} \cdot 100\% \] (6)

where \( m(pr) \) is the practical mass of the coating; \( m(th) \) is the theoretical mass of the coating, which should have been obtained in accordance with the Faraday law. Since the vanadium content did not exceed 0.22%, it was not taken into account.

As can be seen from Table 3, the current output at low temperatures of the electrolyte is lower than at high temperatures. This is due to the fact that at a temperature of 90°C, the coating is not only increased by electrolysis, but also because of the chemical reactions of the reduction of nickel and vanadium ions with sodium hypophosphite, so the current efficiency in these cases exceeded 100%. The quality of the coating, first of all, improved with an increase in the temperature of the electrolyte and the concentration of sodium hypophosphite, and also with a decrease in the concentration of boron nitride.

To study the wear resistance coating on the sample was applied from electrolyte No. 1 with additives of sodium hypophosphite 30 g / l and boron nitride 50 g / l. The electrolyte temperature was 90 °C, the cathode current density was 1A / dm². The heat treatment of the coated sample was carried out at a temperature of 600 °C for 1.5 hours. Wear of this coating was 3.9 × 10^-6 g / m. For comparison, a steel sample was tested synchronously with a heat-treated chemical nickel-phosphor coating deposited from an acetic acid solution with sodium hypophosphite as a reducing agent [3-8]. The wear of nickel-phosphoric coatings was more than 6.7 times.

4. Conclusion

It is shown that, due to the introduction of vanadic acid and boron nitride into the electrolyte, the wear resistance of coatings increases. The resulting regression equations make it possible to calculate the micro hardness of the coatings when the composition, the temperature of the electrolyte and the heat treatment temperature change. The composite coating of nickel-vanadium-phosphorus-boron nitride can be recommended for increasing the resistance of deforming tools, especially molds operating at temperatures up to 600°C.

Reference

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