Coloristic properties of decorative aluminum coatings applied by cold gas dynamic spraying (CGDS)

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Abstract. When making objects of environment design with metal coatings, it is important to consider not only the protective properties of the coatings, but also the decorative ones. The use of aluminum CGDS coatings with subsequent tinting on metal environment design castings will not only increase the corrosion resistance of artistic products, but also give them new aesthetic qualities.

1 Introduction

The use of protective and decorative coatings for environment design objects made of metal allows to solve many problems in the field of technical aesthetics and design. In the production of environment design objects made of metal, it is important to consider not only the protective properties of the coatings used, but also the decorative ones.

2 Materials and methods

One of the methods of applying protective coatings is the method of cold gas-dynamic spraying [1-5]. The advantage of this method is the low temperature during spraying, which eliminates the deformation of the product. The method makes it possible to apply coatings both on limited parts of products and on surfaces of considerable size, as well as to give them the necessary protective and decorative properties [6-8]. Standardized powder materials produced by Obninsk Powder Spraying Center are used for spraying. When evaluated visually, sprayed aluminum coatings are not distinguished by a wide range of colors. To enhance the color performance of the sprayed aluminum coatings, chemically active toning solutions were used. Studies have shown [9] that the use of these the toning compositions allows expanding the color palette of aluminum surfaces, but there is no information on the use of chemically active compositions on the sprayed surfaces, which confirms the relevance of this study. Toning of aluminum coating will allow to obtain a color from bronze to dark brown color depending on the time of exposure to chemical solutions [10].

The study selected a powder material of grade A-30-01 containing 70 % aluminum and 30 % corundum. The presence of corundum in the powder contributes to the best anchoring

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of particles on the surface. The coatings were applied to 40x20 mm metal substrates. Sputtering speed 0.5-1 m/s, heating temperature 400-500°C, powder dispersion 15-25 microns. The toning compositions used in art processing of metals have been determined for toning of aluminum CGDS coatings [6-10]. Detailed formulations of chemical compositions are presented in Table 1.

<table>
<thead>
<tr>
<th>Sample number</th>
<th>Chemical formulations</th>
<th>Color of coatings</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cobalt acetate, 50 g/l Kalium permanganate, 25 g/l</td>
<td>Bronze Brown</td>
</tr>
<tr>
<td>2</td>
<td>Orthophosphoric acid, 40 g/l Fluoride potassium, 3 g/l Chrome (VI) oxide, 5 g/l</td>
<td>Gray-green</td>
</tr>
<tr>
<td>3</td>
<td>Chrome (VI) oxide, 3 g/l Sodium silicon fluoride, 3 g/l</td>
<td>Golden</td>
</tr>
</tbody>
</table>

The solutions were applied to mechanically treated samples. For best results and most even tone formation, and to investigate the effect of roughness on color, the sample surface was machined to a certain roughness range of Ra, microns and Rz, microns using an abrasive tool.

The quantitative component of color [11-14] was determined using a Gretag Macbeth Spectroeye spectrophotometer on surfaces with a roughness range of 0.3-6.3 microns.

X-ray structural analysis was performed to determine the structural components of the toned coatings. The combined coating samples were imaged using an ARL X'tra diffractometer (serial number 135).

### 3 Results and discussion

The effect of surface roughness Ra between 0.399 microns and 6.322 microns on gloss was investigated. On the untreated aluminum surfaces with roughness Ra 6.322 microns the gloss was 7%, on the polished surfaces with roughness Ra 0.399 microns - 25%. We determined the class of surface cleanliness in accordance with GOST 2789-59 [15]. Experimental data are shown in table 2.

<table>
<thead>
<tr>
<th>Sample number</th>
<th>Surface treatment</th>
<th>Ra. microns</th>
<th>Rz. microns</th>
<th>Shine. %</th>
<th>Surface finish class (according to GOST 2789-59)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Surface without treatment</td>
<td>6.322</td>
<td>36.446</td>
<td>7</td>
<td>4</td>
</tr>
<tr>
<td>2</td>
<td>Silicon carbide M63</td>
<td>3.995</td>
<td>22.039</td>
<td>10</td>
<td>5</td>
</tr>
<tr>
<td>3</td>
<td>Silicon carbide M28</td>
<td>3.54</td>
<td>18.06</td>
<td>10</td>
<td>5</td>
</tr>
<tr>
<td>4</td>
<td>Silicon carbide M20</td>
<td>3.120</td>
<td>17.824</td>
<td>10</td>
<td>5</td>
</tr>
<tr>
<td>5</td>
<td>Silicon carbide M14</td>
<td>3.092</td>
<td>17.772</td>
<td>10</td>
<td>5</td>
</tr>
<tr>
<td>6</td>
<td>Silicon carbide M7</td>
<td>2.018</td>
<td>12.059</td>
<td>12</td>
<td>6</td>
</tr>
<tr>
<td>7</td>
<td>Polishing</td>
<td>0.399</td>
<td>2.833</td>
<td>25</td>
<td>8</td>
</tr>
</tbody>
</table>

Toning solutions was applied with a brush, at an operating temperature of 25 °C and 60 °C.

We determined the dependence of the effect of the temperature of the solution on the color characteristics. The results showed that the solution of cobalt acetate and potassium
permanganate allowed to tone aluminum coatings in color from bronze to black and brown depending on the concentration and temperature of the solution. Tests were conducted with heated solution #1 containing 50 g/L of cobalt acetate and 25 g/L of potassium permanganate while varying the duration of exposure time on the samples.

Analysis of the results of studies after application of the toning composition showed that the use of chemically active compositions at 60 °C tinted aluminum coatings in the color from dark brown to black. Using the Lab chromaticity coordinates, the luminosity L was determined. Analysis of the spectrophotometric results showed that the L coordinates varied from 37.32 to 12.32, which corresponds to a dense dark-colored coating.

Application of similar compositions at 25 °C allows you to get a gold-bronze shades and vary the intensity of the duration of exposure to the solution (Table 3).

To enhance the color properties, the aluminum coatings were also treated with solutions of phosphoric acid with potassium fluoride and chrome (VI) oxide for greenish hues and with a solution of chrome (VI) oxide and sodium silica for golden hues.

Analysis of the results showed the possibility of expanding the coloristic properties of sprayed aluminum coatings by applying chemically active solutions. The results of the effect of compositions on the color of aluminum sputtered coatings, depending on the exposure time and surface roughness are presented in Table 3.

The color change of aluminum coatings upon application of chemically active solution No. 1 occurred according to the following chemical reactions (1, 2):

\[
\text{Co(CH}_3\text{COO)}_2 + 2\text{KMnO}_4 + 2\text{H}_2\text{O} = \text{CoOOH} + 2\text{MnO}_2 + 2\text{CH}_3\text{COOK} \quad (1)
\]

\[
\text{Al} + \text{KMnO}_4 + 2\text{H}_2\text{O} \rightarrow \text{K(Al(OH))}_4 + \text{MnO}_2 \quad (2)
\]

The dark color of the coating on aluminum can be explained by the course of two redox reactions with potassium permanganate and with cobalt acetate between metallic aluminum. The formation of compounds CoOOH and MnO2 corresponds to a dark brown color.

<table>
<thead>
<tr>
<th>Sample number</th>
<th>Composition of the reagent</th>
<th>Exposure time. min</th>
<th>Roughness surface. Ra. microns</th>
<th>Sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1. Cobalt acetate. 50 g/l</td>
<td>10</td>
<td>5-7</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Kalium permanganate. 25 g/l</td>
<td></td>
<td>2-4</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td></td>
<td></td>
<td>0.1-1</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>20</td>
<td>5-7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>2-4</td>
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<td></td>
</tr>
<tr>
<td>6</td>
<td>0.1-1</td>
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</tr>
<tr>
<td>7</td>
<td>30</td>
<td>5-7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>2-4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>0.1-1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>2. Orthophosphoric acid. 40 g/l</td>
<td>5</td>
<td>5-7</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>Fluoride potassium. 3 g/l</td>
<td></td>
<td>2-4</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>Chrome (VI) oxide. 5 g/l</td>
<td></td>
<td>0.1-1</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>7</td>
<td>5-7</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
To identify the structural components on the surface of the coating, an X-ray structural analysis was performed. The Al₂O₃ phase (2θ angles: 25.6°; 35.17°; 37.76°; 43.35°; 52.59°; 57.5°; 66.54°; 68.27°) is quite clearly visible in the X-ray diagram shown in Figure 1.

Fig. 1. X-ray of the sample with spraying of aluminum powder A-30-01 and subsequent tinting with cobalt acetate and potassium permanganate solution (solution №1).

The reaction after the application of solution number 2 was according to formula (3):

\[ \text{CrO}_3 + \text{Al} + \text{KF} + 2\text{H}_3\text{PO}_4 = \text{CrPO}_4 + \text{CrF}_3 + \text{AlPO}_4 + 3\text{H}_2\text{O} \]  \hspace{1cm} (3)

The formation of CrPO₄ compounds corresponds to black, CrF₃ to green, and AlPO₄ to white flecks.

The effect of solution number 3 on the color is presented as a chemical reaction (4):

\[ 2\text{CrO}_3 + 2\text{Al} + 3\text{Na}_2[\text{SiF}_6] = 2\text{CrF}_3 + 2\text{Na}_3[\text{AlF}_6] + 3\text{SiO}_2 \]  \hspace{1cm} (4)

The coloristic components were measured in Lab, XYZ and RGB color models, which determine the color value of the three components.

Quantitative color values of sprayed aluminum coatings as a function of toning solution composition, exposure time and roughness are presented in Table 4.
We determined the effect of the time of exposure to the solution depending on the temperature of its heating and the roughness of aluminum coatings on the L lightness. Analysis of the results showed that the luminosity varies from 40.54 to 80.44 on surfaces with a roughness range of Ra 5-6.3 microns, from 43.76 to 80.2 on surfaces with a roughness range of Ra 2-4 microns and from 42.2 to 80.25 on surfaces with a roughness range of Ra 0.3-1 microns. The results of the analysis are shown in Figures 2 - 4.

According to the coloristic data Lab determined the effect of toning compositions on the L luminosity. The results of comparative analysis at roughness Ra = 5 - 6.3 microns showed that the color lightness on the sample coated with the reagent №3, consisting of chrome (VI) oxide and sodium silicon fluoride at different times of exposure and temperature 25 °C gives the highest index L. The samples coated with cobalt acetate and potassium permanganate showed the lowest L values, which confirms the formation of compounds CoOOH and MnO2 on aluminum surfaces.

As a result of this experimental research, the possibility of using an alternative method of color measurement, which involves mobile measurements in the field, having only a
smartphone from the equipment, which is very convenient in today's realities. To adapt this method, it is necessary to develop measures to create standard conditions for measurements, as well as the ability to reproduce the required conditions. The primary sample of this method gives results comparable with those obtained with a spectrophotometer. At the same time, the nature of the deviations suggests that the results from the smartphone can be corrected, interpolated, and then serve as a valid alternative to the spectrophotometer measurements.

According to the coloristic indicators of the RGB color model, we determined quantitative values for each color component. As a result, the maximum values of each of the color index components after exposure to chemically active compositions depending on the surface roughness were revealed. The maximum values of \( R = 225 \) and \( G = 195 \) are reached after the application of composition № 3 with the formation of chrome fluoride, the exposure time of 8 minutes at a roughness of 5 - 6.3 microns; the value of \( B = 170 \) is also reached after the exposure of the solution № 3 on a polished surface.

4 Conclusion

Studies of changes in the color components RGB, Lab, XYZ (Table 4) depending on the surface roughness have shown that the surface cleanliness directly affects the color of coatings. According to the data of the table it is possible to determine the chemical composition of the solution, at the application of which the index of the color component is characterized by its maximum value. Analysis of Lab values for aluminum coatings makes it possible to determine that the L coordinates, showing the color lightness, vary depending on the tinting compositions and technological modes of their application. X-ray analysis made it possible to identify the formation of chemical compounds directly affecting the color of the coatings and identify them.

Conclusions:

1. To assess the decorative properties, the parameters of the coating that directly affect its visual perception were identified. Among these are shine, surface color, reflectivity and roughness value. These parameters were considered and evaluated on aluminum surfaces;
2. The effect of the roughness of the coated layer of environmental design objects on the reflectivity of CGDS coatings made of aluminum was established;
3. Quantification of color coordinates provided an opportunity to reliably determine color in the design and restoration of products with specified color parameters;
4. Known recipes for patinating and coloring compositions have been tested, by adjusting the exposure time and concentration of which, it is possible to achieve different effects on aluminum coatings obtained by cold gas-dynamic spraying. Thus, it becomes possible to combine the manufacturability of any metal and the noble shades of bronze in one artistic product, also providing protection for the castings from the effects of aggressive urban environment;
5. As a result of the work the basic technological parameters of the color tinting of aluminum coatings in order to obtain the color characteristics imitating brass and bronze, used in the design and restoration of artistic products have been determined.
Fig. 5. Reagent compositions, curing times, roughness and color of aluminum coatings.

References