Surface free energy of zinc coating after finishing treatment

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Protective properties of zinc coating increase with an additional coating such as: chromate, phosphate, paint and polymer coating. Besides, additional treatment of zinc coating serves decorative purposes as well. The paper presents the influence of additional coating of zinc coating on their adhesive properties which are especially helpful in processes where adhesion plays an essential role. These processes include among others: gluing, painting or varnishing. Adhesive properties are characterized by the value of surface free energy.

Key words: *surface free energy; adhesive properties*

1. Introduction

Surface free energy usually determines surface energetic state (adhesive properties) of construction materials. It is of great importance in such technologies as gluing, sealing, painting, printing, decorating, and in many others, where adhesion plays an important role.

The objects of tests and analyses are galvanic zinc-coated sheets after various finishing treatments applied in electrolytic zinc coating processes. The latter process is one of the future directions of development in electroplating. The aim is to produce in advance an additional coating on a covered coating. Electrolytic (galvanic) coatings are covered by organic layer (coating) through ion implantation, laser treatment or other methods to achieve significant improvement of electrolytic coating consumption properties or to obtain new coating properties. In many cases, additional treatment increases protective or decorative values. Very often additional treatments combine both these functions.

The finishing treatments such as chromate and phosphate coating, as well as special chemical treatment were analyzed. They were used to smoothen the coating (which requires etching in a bath of sulfuric acid and chromium trioxide).

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In terms of the adhesion theory, it is interesting whether the analyzed treatments have any important influence on the value of surface free energy, used as thermodynamic index of adhesive properties.

A comparison between polar and dispersion components of the surface free energy after finishing treatments is also interesting. It shows essential changes of polar component of surface free energy. These changes strongly influence a possibility of improving adhesive properties, in particular high-strength bonding join.

2. Theory

Surface free energy (γ_S) as one of the thermodynamic quantities describing equilibrium of atoms within the upper material layers, reflects specific unbalanced state of intermolecular interactions occurring at the surface phase between two media, being the characteristic feature of each material [1].

There are many methods to determine surface the free energy [1–5]. They are based on determination of dispersion and polar components according to the Berthelot hypothesis that the intermolecular interaction between molecules of two different materials is equal to geometric mean of the interactions between molecules.

In the paper, the surface free energy was determined by the Owens–Wendt method, one of the most popular methods to determine γ_S of solids. The polar and dispersion components of surface free energy were determined according to the following equations [4]:

$$\left(\gamma_s^d\right)^{0.5} = \frac{\gamma_d\left(\cos\Theta_d + 1\right) - \sqrt{\dfrac{\gamma_d}{\gamma_w}}\gamma_w\left(\cos\Theta_w + 1\right)}{2\left(\sqrt{\gamma_d^{\,d}} - \sqrt{\gamma_d^{\,p}\dfrac{\gamma_w^{\,d}}{\gamma_w^{\,p}}}\right)} \tag{1}$$

$$\left(\gamma_s^p\right)^{0.5} = \frac{\gamma_w\left(\cos\Theta_w + 1\right) - 2\sqrt{\gamma_s^{\,d}\gamma_w^{\,d}}}{2\sqrt{\gamma_w^{\,p}}} \tag{2}$$

where: γ_s^d – dispersion component of the surface free energy, γ_s^p – polar component of the surface free energy, γ_d – the surface free energy of diiodomethane, γ_d^d – dispersion component of the surface free energy of diiodomethane, γ_d^p – polar component of the surface free energy of diiodomethane, γ_w – the surface free energy of water, γ_w^d – dispersion component of the surface free energy of water, γ_w^p – polar component of the surface free energy water, Θ_d – contact angle of diiodomethane, Θ_w – contact angle of water.

3. Experimental

Zinc coatings are widely used for steel and cast iron corrosion protection. Zinc coated steel elements are relatively cheap, and in many cases this is the most effective corrosion protection [6, 7]. Zinc coatings are susceptible to darkening and spotting when touched. White rust appears on the surface during storage. That is why an additional treatment to protect zinc coatings surface is recommended [8]. Some finishing treatments are chromate coating, phosphate coating, painting, covering coatings of different resins, UV exposure and others [6, 8]. One of them is also a special chemical treatment in order to smoothen the coating (which requires etching in a bath of sulfuric acid and chromium trioxide). Another is adding a brightener to the galvanizing bath (glossy zinc coating).

Previously, the galvanizing (zinc coating) with glossing had more applications. Glossy zinc coatings, additionally coated by blue chromate coating can replace (in same applications) Cu–Ni–Cr decorative coatings, particularly when gloss life limitations and economical issues are important. Because of deficit and high cost of nickel (Ni), decorative zinc coatings are more and more popular in industry [6, 9].

Chromate treatment. In most cases, chromating is used to improve anticorrosive properties, in particular by increased electrochemical corrosion resistance [6, 8, 10, 11]. It requires creation of a thin passive layer. Corrosion resistance of a zinc coating can increase from 8 to 10 times after passivation in a proper bath [10]. Chromate coating (especially thicker) is characterized by some porosity. It creates a good ground coat under various kinds of paints, combining with ground and mechanical bonding, when penetrating in pores. Chromate ground protects zinc coating effectively in the caseof minor paints spalling. Chromate treatment is very often carried out directly after galvanizing. Protective properties of the chromate coating do not deteriorate in result of mechanical damage of the passive layer (e.g. scratches), due to so-called secondary passivation [8]. Chromate treatment can be applied together with brightening (glossing).

Phosphate treatment. Phosphate treatment can be carried out to seal and increase paint adhesion with zinc coating. It was proved that adhesion of non-metallic coatings to a pure zinc coating is less effective, than to zinc coating, which was chromated or phosphated [8].

Organic coatings. Coatings of different paints and resins are often used in addition to zinc coatings. These coatings are corrosion protective [12, 13]. It was proved that zinc coating's durability is 25–30% longer than the durability of coatings used separately. Steel protective system – zinc coating and paint coating is defined in literature as "Duplex" [7, 14, 15]. Protective period of Duplex system is longer than the sum of protective periods of these coatings used individually. A proper choice of paint coating is a fundamental problem in additional zinc coating protected by paint coating.

Recommendations for varnish products selection for painting zinc coatings and zinc coating treatments before covering paint coatings can be found in literature [15]. Hardenable polymers (polyester, melamine, acrylic, phenolic-formaldehyde and others) are very often used as organic coatings which cover zinc coatings. Better adhesion of the non-metallic coatings to zinc coatings which were phosphated or chromated, than to pure zinc coating can be noticed. Moreover, in the case of pure zinc coating there may appear corrosion products between this coating and the covering medium (especially if it is of acidic character). These corrosion products weaken the joint. That is why it is advantageous to use phosphate or chromate coatings which inhibit zinc corrosion and improve paint coating adhesion. Sometimes the semi-finished product (after zinc treatment and cooling) is covered by resin water emulsion, for example styrene-butadiene resin. Then the resin layer is formed on zinc surface. Its hardness is comparable with that of chromate coating hardness or even exceeds it.

Ultraviolet radiation exposure increases zinc coating protection as a result of special zinc variation coating. It has a higher durability and resistance than a typical variation [6, 8].

3.5. Testing materials

The research was carried out on the zinc galvanic (electrolytic) tests (sheets) subject to various technological operations. These operations create additional coatings on zinc coatings.

The following tests were used:

• the zinc galvanic sheets (about 1,00 sheet gauge) which were galvanized in cyanoalkaline bath, without any special chemical treatment, zinc coating thickness equal to about 10 μm/side,

• the zinc galvanic sheets (about 1,00 sheet gauge) which were galvanized in cyanoalkaline bath, with a special chemical treatment in order to smoothen the coating, zinc coating thickness equal to about 10 μm/side,

• the zinc galvanic sheets (about 1,00 sheet gauge), which were galvanized in cyanoalkaline bath, with chromate treatment, equal to about 10 μm/side zinc coating thickness,

• the zinc galvanic sheets (about 1,00 sheet gauge), which were galvanized in cyanoalkaline bath, with photosphate treatment, zinc coating thickness equal to about 10 μm/side.

3.6. Measurement method

Surface free energy value was determined using the Owens–Wendt method. The measurements of the contact angle Θ of testing materials were carried out to calculate the surface free energy. The method uses a direct measurement of the contact angle

formed between a droplet of a measuring liquid and the testing surface. Two reference liquids of specified values of both surface tension, polar and dispersion components of the surface free energy were employed: distilled water, which is strongly polar (its polar component is equal to 51 mJ/m^2 at the total free surface energy amounting to 72.8 mJ/m^2) was used as a dipolar liquid, and diiodomethane as an apolar one. The components of free surface energy for diiodomethane are respectively: polar – 2.4 mJ/m^2 and u-mode – 50.8 mJ/m^2 [1, 4].

The components γ_S^d and γ_S^p for tested materials can be calculated from the Eqs. (1) and (2).

4. Results

The obtained surface free energies of galvanic zinc coated sheets were presented in Table 1.

Table 1. Surface free energies and their components of galvanic zinc coated sheets

No.	Finishing treatment of galvanic zinc coated sheets	Surface free energy [mJ/m^2]		
		γ_S	γ_S^p	γ_S^d
1	Galvanizing in cyanoalkalline electrolyte	70.8	47.9	22.8
2	Galvanizing in cyanoalkalline electrolyte with special chemical treatment – coat smoothing	68	42.6	25.4
3	Galvanizing in cyanoalkalline electrolyte with chromate treatment (passivation)	41.7	8.6	33.1
4	Galvanizing in cyanoalkalline electrolyte with phosphatizing (passivation)	50.8	16.3	34.5

The highest surface free energy, among the tested samples, was obtained in the case of galvanizing in cyanoalkalline electrolyte (70.8 mJ/m^2), while the lowest – after chromate treatment (41.7 mJ/m^2). It can be noticed that the use of additional coating causes a significant reduction of the surface free energy in two cases (out of three tested). Moreover, the adhesion properties of chromate and phosphate coated surface deteriorates when compared to zinc coating surface without finishing treatment.

The relation between dispersion and polar parts of the surface free energy is also interesting. In the case of zinc coating without additional coating and with a special chemical treatment (in order to smoothen the coating) the polar component γ_S is almost twice larger than the dispersion component. For the zinc coating with chromate and photosphate passivation, the relation is opposite.

In the case of chromate treatment γ_S^p (8.6 mJ/m^2) is almost four times smaller than γ_S^d, the latter amounting to 33.1 mJ/m^2. After phosphatizing the polar component γ_S^p

is equal to 16.3 mJ/m^2 and the dispersion component value is 34.5 mJ/m^2. The former component is thus twice smaller.

The contribution of individual components to the surface free energy depend, among other things, on the kind of forces acting between atoms and molecules of the analyzed materials. The kind of forces depends mainly on the chemical structure of the material and external factors (e.g. temperature).

Dispersion forces are of a universal character and occur in all elements. This is why they always contribute to the surface free energy value. The polar component (including interaction derived orientation forces as well as inductive forces, for the sake of their character) can occur in specific conditions and its contribution may vary. Probably in the zinc coating (in particular in the zinc coating surface layer) polar interaction participate to a higher extent than in chromate or phosphate coatings. It is also possible that more polar molecules occur which are able to create polar forces.

It should also be noticed that the change of obtained values γ_S^p in function of finishing treatments procedure is considerably higher than the dispersion component γ_S. It is thus supposed that the polar component is more "sensitive" to the chemical composition of the material surface layer.

5. Summary

Based on the results reported in the paper, it can be noticed that the application of an additional finishing treatment of zinc coatings (which requires forming additional phosphate and chromate coatings) changes in the adhesive properties, as compared to zinc coatings without the additional treatment, decreasing their surface free energy value. In principle, our results contradict the published data stating that chromate and phosphate coating improve adhesion of, e.g. paint coating to zinc coating. Based on the obtained experimental results, a relation opposite to the published information was noticed for the samples and procedures employed in this work. Probably the reason was that the tested surface was oiled in order to protect it during transportation.

The changes of polar components of surface free energy are very interesting. After the finishing treatment, the value of this component is significantly reduced as compared to the value of galvanic zinc. Moreover, in the case of zinc coatings without finishing treatment and after a special chemical treatment (in order to smoothen the coating) the polar component value is twice larger than the dispersion component. As a result of other finishing treatments (chromating and photosphating), the polar component value is smaller: its value after photosphating is twice lower, and after chromating four times lower.

In the future, it could be extremely interesting to carry out more detailed analysis of the noticed differences between surface free energies and the data published in literature.

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