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Molybdenum protective coatings adhesion to steel substrate

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Abstract. Protection of the critical parts, components and assemblies from corrosion is an urgent engineering problem and many other industries. Protective coatings' forming on surface of metal products is a promising way of corrosionprevention. The adhesion force is one of the main characteristics of coatings' durability. The paper presents theoretical and experimental adhesion force assessment for coatings formed by molybdenum magnetron sputtering ontoa steel substrate. Validity and reliability of results obtained by simulation and sclerometry method allow applying the developed model for adhesion force evaluation in binary «steel–coating» systems.

1. Introduction

Corrosion resistance of metals has a direct impact on the product's performance. A corrosion losses in countries with developed industry is up to 5% of gross national product (GNP) [1]. Protective coatings' formation on metal surface relates to methods of corrosion control [2–5]. High adhesion between coating and substrate is one of the major criteria for coatings' material selection. At high coating strength and low adhesion to the substrate coatings' detachment and disconnection occurs. At low coating strength the bubbles with a gap appear which dramatically increases the rate of metal oxidation.

Definitely, other problems related to the protective coatings application can be indicated, however, and they are reduced to wrong coatings' material selection. Qualitativemethods of adhesion evaluation include mechanical (scratch test, a test of abrasion resistance, tensile strength) as well as non–mechanical methods (XRD) [6].XRD is usedfor stress state investigation of polycrystalline coatings (e.g.molybdenumcoatings)deposited by magnetron sputtering [7]. Application of this method allows carrying out an estimation of residual stresses that have a direct impact on adhesion of molybdenum coating to the substrate [8–16]. Among the quantitative methods of adhesion evaluation allocate sclerometry, nanoindentation [17] and scribing as the most widespread in applied research of coatings'adhesive resistant [18].Scientific and practical interest of thin molybdenum coatings formation is causedby its heat resistance, high mechanical strength and unique electrical properties.Molybdenum is used as a material for the manufacture of contact groups and protective layers in integrated circuits [19]and thin–film solar cells [20, 21], superconducting thin films [22] and optical interference coatings [23]. Magnetron sputtering of refractory metals including molybdenum is used for wear–resistant anticorrosive coatings formation in various fields of industry [24, 25].

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2. Materials and methods

J24056 grade steel is used as a coating's substrate. Products made of this steel operating under high temperatures conditions and corrosive environments that promote corrosive wear. The study assesses experimentaladhesion force (σ) of molybdenum coating to substrate (defined as the interaction force between coating and substrate per unit area, Pa) obtained by sclerometry in comparing with calculation results of developed model. Theoretical calculations can be used for service life evaluation of coated products operating at elevated temperatures in corrosive environments.

This paper describes the adhesion force by sclerometry. At adhesion force determination by this method the coating breaking occurs to baring a substrate with it following detachment. It must be an accurate measurement horizontal load, crack width, the film thickness and hardness to quantify the adhesion value. Horizontal force F was measured during coating's scratching at such vertical load when the substrate remained clean on indenter track. It was assumed that horizontal force F (1) is the sum of three components. The first component, F_1 is the force that occurs when coating is scratching (2). The second component, F_2 (3) is the force that provides full coating's scratching from the substrate. The third component, F_3 is the force acting on indenter while it moves across substrate without coating:

$$F = F_1 + F_2 + F_3 \tag{1}$$

$$F_1 = dhH \tag{2}$$

Here d is the track width, h is the film thickness, H is the hardness of coating.

$$F_2 = 1/4\ (\sigma\pi d^2) \tag{3}$$

Here σ is the adhesion force, determined by equation:

$$\sigma = 4(F - F_3 + dhH)\ /(\pi d^2) \tag{4}$$

Experimental installation for adhesion determination has been collected on the basis of Vickers' hardness tester «PMT–3M». A horizontal force is applied to the rotating platform and the microhardness was determined using a strain gauge. The following analysis of indenter track was performed by using scanning electron microscopy (JEOL JCM–5700). Determination of adhesion properties of the coating was carried out with a vertical force 0.5 N applied to indenter.

3. Results and discussion

Experimental scheme for the adhesion force research is shown on figure 1.The indenter track and the width scratch for randomly selected area is shown on figure 2a. The initial parameters'values are the track width (d=23 mm), coating hardness (Hv=450), coating thickness (h=1 mm) and the difference between horizontal forces (F_1–F_3=0.45 N). Side micrograph of the diamond indenter is shown on figure2b. Top micrograph of the diamond indenter is shown on figure 2c.

The adhesion force value calculated by equation (1) gives the result equal to σ=760 MPa. Coincidence of adhesion force evaluation for a magnetron sputtered «steel–molybdenum coating» system with values, obtained earlier by authors, leads to conclusion about reliability of the developed measurement techniques.

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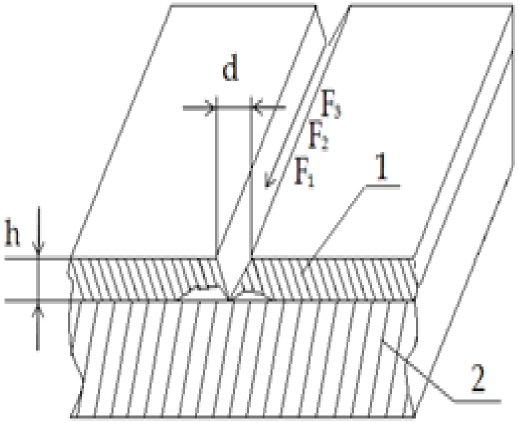
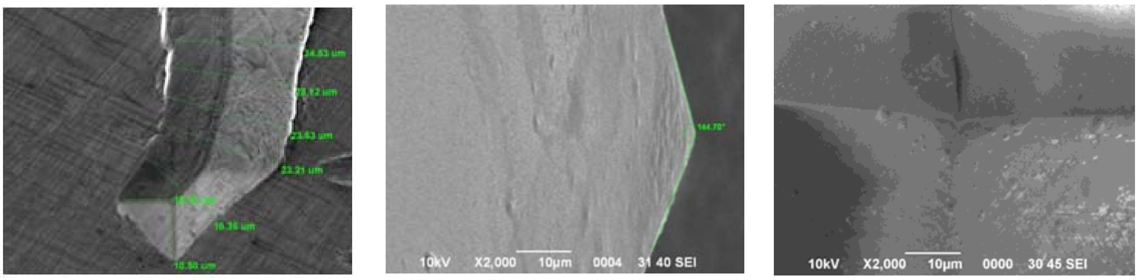


Figure 1. Cross–sectional scheme of the scratch (1–coating; 2–substrate).



a b c

Figure 2.SEM images: a – track of indenter on the surface of molybdenum coating; b – side micrograph of the diamond indenter; c – top micrograph of the diamond indenter.

An example of adhesion force calculation for molybdenum coating obtained by magnetron sputtering onto the surface of J24056 grade steel is considered to verify received results. For the adhesion force calculation,it is applied an approach described for magnetron sputtered coatings in reference [26]. The adhesion force could be calculated by equation:

$$\sigma = kNf \tag{5}$$

Here k is the dimensionless coefficient that takes into account the reduction of possible bonds number, depending on the presence of structure defects; f is the strength of a single metallic atoms' bond near the border of «steel–coating» transition layer; N is the atoms' distribution through the layer depth with thickness in order of the lattice constant.Transition layer is a substitutional solid solution, in this case it is appropriate to describe its contribution to adhesion force by each material with equation (6):

$$\sigma = \sigma_1 + \sigma_2 = kN_1 f_1 + kN_2 f_2 = k(N_1 f_1 + N_2 f_2) \tag{6}$$

Here f_1, f_2 is the strength of a single metallic atom bond of each material (N); N_1, N_2 is the each material atoms' distribution of through the layer depth with thickness in order of the lattice constant and one square meter area. With regard to the number of atoms in crystalline lattice of the target layer it was found the depth distribution $N_1(x)$, $N_2(x)$ of transition layer:

$$N_1 = C_1 N_0; \quad N_2 = C_2 N_0 \tag{7}$$

The single bond force of the atom was calculated using the material melting point (T). An average kinetic energy of random atoms' motion at such temperature goes into overcome work of the interatomic attraction forces thus this process can be represented by equation:

$$3/2\ k_B T = nfd \tag{8}$$

Here k_B is the Boltzmann constant; *n* is the number of overcoming atomic bonds in crystal lattice and *d* is the lattice constant.
Thus for calculation of the atoms' single bond force can be used the following expression:

$$f = (3/2\ k_B T) = (2nd) \tag{9}$$

The adhesion force σcan also be estimated through the adhesion energy:

$$W_a = (W_{p1} W_{p2} (K_1 + K_2)^2) / (W_{p1} K_1^2 + W_{p2} K_2^2) \tag{10}$$

Here W_{p1} and W_{p2} is the surface energy of contacting materials (reference values) that can be also calculated by method described in [26]; K_1 and K_2 are the coefficients calculated by equation:

$$K_1 = \frac{\upsilon_1}{(1 - \upsilon_1)}; \quad K_1 = \frac{\upsilon_1}{(1 - \upsilon_1)} \tag{11}$$

Here υ_1 and υ_2 are the Poisson's coefficients of contacting materials. Thus the estimated formula for adhesion force σ has a form:

$$\sigma = (W_a E)^{1/2} / (\pi h)^{1/2} \tag{12}$$

Here *E* is the elasticity modulus of surface material.The impurity content dependence from the depth of transition layer in «molybdenum–steel» system calculated on the basis of mass transfer model [27, 28]. Interatomic forces calculated for iron and molybdenum correspondently received the following values: f_1=3.76·10^{-11} N and f_2=5.98·10^{-11} N. The adhesion force is also influenced by purity of product's surface, by presence of impurities and defects in it, and can also be influenced by various other factors. Adhesion force measurements show that as a result of these factors a contact area of coating is 45%...50% less than surface area on which the coating is applied to by magnetron sputtering [18]. Because of this reason it is used a coefficient *k*=0.5for adhesion force modeling calculations.
The coating's adhesion force σ calculated by equation (5) based on iron and molybdenum atoms' distribution through the depth of transition layer is presented on figure 3. There is a slight discrepancy on figure 3 between calculated values of the adhesion force σ compared with the reference: 760 and 820 MN/m^2, so we can assume that calculation results are consistent with published data. Maximum of σ corresponds to the highest concentration of implanted impurity, so when attempting detach the coating, the greatest probability of detachment corresponds to the surface edge or to the depth of 1.02 μm where the transition layer ends.
It should be noted that the estimated value of adhesion force calculated through adhesion energy substantially higher than the experimental data. According to estimation the adhesion force on steel surfaces for coatings with 1 μm thickness can reach about 800 N/m^2, at the same time adhesion of molybdenum coating to the surface of pure iron attains more than 820 N/m^2 [26]. This overestimation of calculated results apparently due to the fact that evaluation model considered perfectly smooth, clean surface without defects.

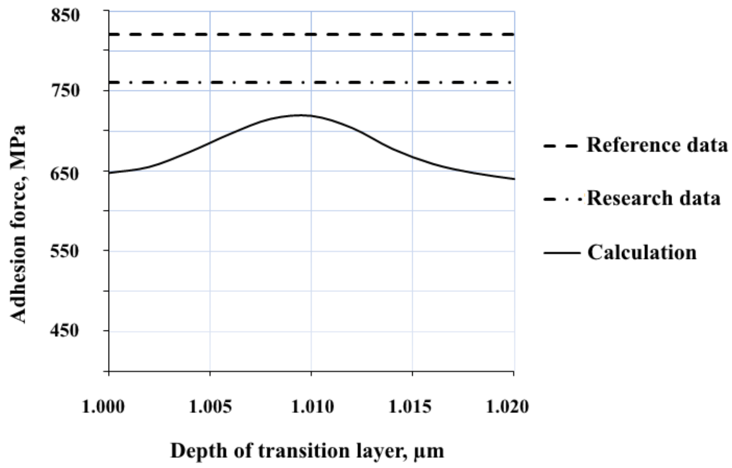


Figure 3. Adhesion force dependence from the depth of «steel–molybdenum» transition layer at 1µm coating's thickness.

The obtained estimationslead to an error of more than 100% due to fact that it is not possible to accurately determine the interaction potential between atoms, so approximate potentials are used: Morse and others.The values of adhesion forceσ will be close to the estimated values if coefficient k=1 will be used in the proposed model (ideal case).

4. Conclusion

This investigation assessestheadhesion force between molybdenum coating deposited by magnetron sputtering and J24056 grade steel substrate, which is amounted of 760 MPa from the experimental data.The developed model is used for adhesion force evaluation of thin–film coatings and calculation results show that the minimum adhesion force is equal to 650 MPa.

The results of adhesion force calculation are in satisfactory agreement with reference and verified with experimental data. Thus, the proposed model can be used in the adhesion force evaluation for the binary «steel–coating» systems.

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