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**Упрочнение гальванических покрытий наночастицами:  
одномерная модель суперпозиции**

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**Аннотация.** Предложена эвристическая модель упрочнения нанокпозиционных гальванических покрытий. Она содержит минимальное количество системных параметров, среди которых микротвердость материала основы покрытия, количество включаемых наночастиц и средний размер зерен, и может служить для оценки предельной твердости покрытий. Модель представляется сводимой к форме уравнения Холла-Петча и допускает прозрачную интерпретацию как структурных основ, так и конечных уравнений. Применение модели к реальному нанокпозиционному гальваническому покрытию на основе хрома позволило получить довольно точное совпадение с данными, определенными экспериментально, с точностью 3,35%. Разработанный подход позволяет получить упрощенные оценки предельной твердости при нанесении нанокпозиционных покрытий, где, например, снижение износа пар трения представляет актуальную проблему.

**Ключевые слова:** композиционные покрытия; гальванические покрытия; наноразмерные частицы; микротвердость; дислокации; упрочнение

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Original article

**Nanoparticle-based hardening of galvanic coatings:  
a one-dimensional superposition model**

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**Abstract.** A heuristical model of hardening the nanocomposite galvanic coatings has been proposed. It contains a minimal number of system parameters among whose are microhardnesses of the base coating material, of nanoparticles to be incorporated and mean grain size, and can serve to estimate the ultimate hardness of coatings. The model appears to be reducible to the Hall-Petch equation form and admits transparent interpretation of both structural basics and final equations. Application of the model to a real nanocomposite galvanic chromium-based



coating resulted in a rather appropriate match with the data determined experimentally, with accuracy of 3.35%. The approach developed gives rise to light estimates of ultimate hardness in nanocomposite coating applications where, e.g., wear reduction in friction pairs represents an actual problem.

**Keywords:** composite coatings; galvanic coatings; nano-dimensional particles; microhardness; dislocations; hardening

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**Introduction.** Recent technological advancements in nanocomposite galvanic coating deposition are well-documented [2, 7, 9–21] and related to a co-deposition of low-dimensional particles, fibres or wires of different nature as to, e.g., carbides, borides, oxides, sulphides, polymer powders etc., proceeding simultaneously to that of the metal cations out of the electroplating bath. So embedded nanophase constituted of SiC, WB, WC, Si<sub>3</sub>N<sub>4</sub>, Al<sub>2</sub>O<sub>3</sub>, BN, TiC, AlN, diamond particles etc., may improve, among others, such physical and mechanical properties of resulting coatings as microhardness, wear and corrosive resistance [2, 7, 9–12, 14–16, 20, 21]. Nanoparticles of different nature produce different impacts on metals in coatings. Thus, embedded WC-nanoparticles significantly improve wear (0.288 mg/cm<sup>2</sup>)<sup>1</sup> and corrosive resistance of nanoNi-based coatings (up to ca. 65,8 kW/cm<sup>2</sup> for the coating with 4 g/L WC in the bath) [10]. Inclusion of Si<sub>3</sub>N<sub>4</sub> resulted in grain fragmentation and related increase of microhardness and corrosive resistance due to dispersion hardening [11]. Microhardness of composite coatings Cr-P appeared to increase from 6.0 hPa up to 9.3 hPa because of nanoAl<sub>2</sub>O<sub>3</sub> embedded whereas corrosion current density decreased from 2.0 down to 0.2 mA/cm<sup>2</sup> as a pure Cr-P alloy was replaced with Cr-P/nano Al<sub>2</sub>O<sub>3</sub> composite coating [16]. Diamond nanoparticles embedded (concentration 8 g/l in the electrolyte, current 3 A/dm<sup>2</sup>) in Ni-coatings provided grain fragmentation and resulting increase in microhardness (up to 5.302 hPa) and wear resistance (friction coefficient 0.1) [7] whereas in [21], microhardness and modulus of elasticity were reported to constitute 4.68 и 194.30 hPa respectively.

However, nanophase optimal concentration in the electrolyte has not been cleared up yet. Physical and mechanical properties of coatings were found to improve with its increase up to a certain threshold [2, 7, 9–12, 14, 15], after which no further improvement or, on the contrary, even some degradation arose [2, 7, 10, 14, 21]. Thus, increase of concentration of nano-WC up to 4 g/l in the electrolyte at nickelizing leads to increase of its content in the resulting coating [10, 21]. Further concentrating the electrolyte reduces nanoWC-content in the coating because of agglomeration. Every particular case seems to be related to the optimal nanoparticle concentration depending on their size, form, physical and mechanical properties etc.

**Materials and methods.** On account of increase in microhardness and wear resistance due to embedded nanoparticles, nano-based coatings appear to be more and more demanded for friction pairs [13, 15, 17, 19]. The reason for this is a direct relation between the wear intensity of a unit consisting of two parts exposed to mutual contact and related friction [3]:

$$I = I'(h(t)) + I''(h(t)) \quad (1)$$

where each item refers to the respective part. Taking into account that, among all possible factors affecting wear the plastic edging and microcutting the metal dominate, either of terms in Eq. (1) can be represented as a sum:

$$I(h(t)) = I_{pe}(h(t)) + I_{mc}(h(t)) \quad (2)$$

In Eq. (2), the plastic edging wear intensity reads [4]:

$$I_{pe}(h(t)) = \frac{1}{V_f} \sqrt{\frac{h_{max}^v}{r}} \frac{\ln^{-t}(1 + \delta)}{2(v + 1)} \left\{ -\ln \left[ 1 - \frac{h_{max}}{r} \left( \frac{q_a}{H} \right)^{\frac{1}{v}} - \sqrt{\frac{2h_{max}}{R} \left( \frac{q_a}{H} \right)^{\frac{1}{v}} \frac{\sigma_s + 2\tau}{\sigma_s - 2\tau}} \right] \right\}^t \left( \frac{q_a}{H} \right)^{1 + \frac{1}{2v}}$$

where  $V_f$  – relative motion speed at friction,  $h$  – microroughness height,  $r$  – contact spot radius;  $v$  – an empirical coefficient depending surface roughness;  $q_a$  – pressure onto nominal square of the contact,

<sup>1</sup> The coefficient of friction was analyzed and the coating weight loss measured. The pin was 3 mm in diameter (Al, 1400 HV), sliding distance 200 m, vertical force 10 N with sliding speed 100 rpm in a nonlubricated condition (the ambient temperature) [10].



$H$  – hardness,  $R$  – microasperity edge rounding radius;  $\sigma_s$  – yield limit;  $\tau$  – tangential strength of a friction bond,  $t$  – an S-N diagram factor;  $\delta$  – the relative permanent strain after rupture.

The microcutting wear intensity is expressed as [4]:

$$I_{mc}(h(t)) = \frac{1}{V_f} \frac{\tan \beta}{2(n+1)} \frac{q_a}{H}$$

where  $\beta$  – angle of the abrasive particle embedding into the part surface,  $n+1$  – the number of cycles resulting in detachment of particles because of wear.

Thus, the asymptotic behaviour of wear intensity at  $H$  big enough is determined by the main term  $\sim H^{-1}$  due to microcutting as the expansion of plastic edging term gives  $\sim H^{-1-\frac{t+1}{2v}}$  which has a lower order of magnitude as  $t$  and  $v$  typically find themselves within the range from 2 to 3 [3, 4, 6].

In general, these expressions illustrate that hardness is of crucial importance for wear intensity of friction pairs. Therefore, ultimate hardness of composite coatings is highly relevant in this sense. Any possibility to perform relevant theoretical estimates can scarcely be overestimated. One could appreciate a light model with a limited number of parameters, which could serve as such a tool. As a minimal general requirement, a model of this kind should contain at least such parameters as microhardnesses of the coating base material and of nano-particles to be incorporated, as well as grain size information. In this paper, we undertake an attempt to develop such a model capable of prognosticating the influence of hard nanoparticles in galvanic coatings on ultimate hardness and, therefore, wear resistance.

**One-dimensional models of the nanocomposite galvanic coating hardening.** Among numerous factors complicating modeling and prognostication of microhardness of galvanic coatings, find themselves, e.g., electrophoretic transfer, diffusion, Brownian motion, sticking, wettability, sedimentation, adsorption, adhesion, electrostatics of particles in the cathode field, collisions of the second phase particles with the crystal pieces being formed, nuclei and other underformed structures, structural defects of the coatings metal (pores, cracks, capillaries, micro-, meso- and macroroughness of the cathode surface) etc. Therefore, treatment of a mean microhardness of nanocomposite coating surface unit would look more promising, provided the microhardness were considered as a compound index encompassing such factors as (i) hardness of the nanocomposite coating on the surface patch small enough to be uniform in the sense of its hardness, and (ii) hardness of the particles to be embedded.

In a number of works [7, 9, 11, 12, 14, 16, 20, 21], relationships between hardness, yield point and metal grain size were established, what enables one to model the process of formation and hardening of nanocomposite coatings. The two mechanisms play the dominating role. They are the dislocation mechanism and grain fragmentation.

Hindrances to dislocation motion are a challenge for further tension growth to promote that. They improve material resistance to external load and can be enforced by both grain edges and nanoparticles uniformly distributed inside the coatings. Should the second phase particles be positioned far enough from one another and incoherent to the matrix, the Orowan mechanism can take place. While sliding because of some tension, the edge dislocation has to overcome periodically varying tension field along the front of uniformly distributed particles. If the particles can be considered as point objects, the tension field in the space between the particles has minima. The dislocation can deflect up to a wave-like form and bypass the particle according to the Frank-Read dislocation generation mechanism. If more dislocations move between the particles, they will leave more Orowan loops around the particle. The dislocation density will then grow and result in formation of a specific regular microrelief and hardening the material what appears to be well expressed by the Hall-Petch equation:

$$H_v = H_g(\sigma_g) + \frac{k}{\sqrt{D}}, \quad (3)$$

where  $H_v$  – material hardness,  $H_g$  – grain hardness,  $\sigma_g$  – internal tension preventing the plastic shear expansion,  $D$  – grain size,  $k$  – a dimensional coefficient.

Grains in polycrystals are neither continuously solid nor perfect but consist of particular sub-grains orientated with respect to one another at some small angles. Their edges prevent dislocation motion, serve as centres of accumulation of impurities what creates particular tension field and contributes to viscosity and both brittle separation probability and yield decrease. The smaller the grains are and the more chaotic misorientation of those exists, the more the polycrystal hardens and resists deformations.



Taking this into account, we employ the idea that in order to harden galvanic coatings by means of low-dimensional (nano-) particles, one has to care of the optimal structure of material through increase of dislocation number and grain fragmentation (Figure 1).

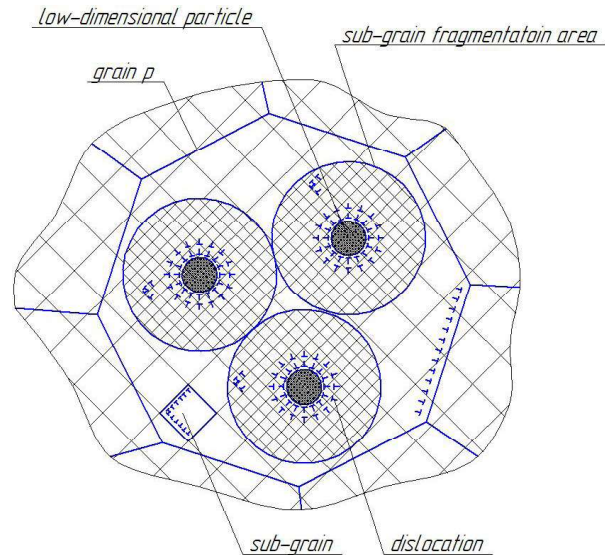


Figure 1 – Schematic representation of how nanocomposite galvanic-chemical coatings form.

Рисунок 1 – Схема механизма формирования нанокomпозиционных гальвано-химических покрытий

*A piecewise-linear model.* We employ a piecewise-linear model (Figure 2) of hardening, whose canvas is the model plane with the set of points  $M_i(l_i, h_i)$ . Within this model, we will consider microhardness of components among whose are particular phases, structural inclusions, grains, thin surface layer (after thermal processing) etc.

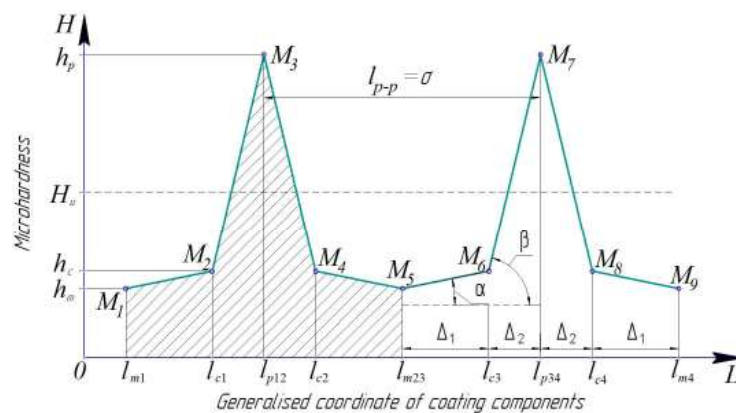


Figure 2 – Schematic presentation of a piecewise-linear model of nanocomposite coating hardening.  $H_u$  – the ultimate hardness of the nanocomposite coating;  $h_p, h_c, h_m$  – microhardnesses of nanoparticles, coating due to grain fragmentation and the basic coating material respectively;  $l_{p-p}, l_{c-p}, l_{m_i}$  – coordinates of their respective  $i$ -th elements;  $l_{p-p}$  – the distance between nanoparticles;  $\alpha$  refers to the slope of segment  $M_5M_6$  (the process of coating hardening due to grain fragmentation) and  $\beta$  to that of  $M_6M_7$  (the process of coating hardening due to dislocation crowding around the nanoparticle);  $\sigma$  – the elementary “cell” length (structure spacing).

Рисунок 2 – Схема линейной физико-математической модели механизма упрочнения нанокomпозиционных покрытий:  $H_u$  – теоретическая микротвердость нанокomпозиционного покрытия;  $h_p, h_c, h_m$  – микротвердость наноразмерных частиц, покрытия вследствие измельчения зерна и основного материала покрытия соответственно;  $l_{p-p}, l_{c-p}, l_{m_i}$  – координаты соответствующих  $i$ -х элементов;  $l_{p-p}$  – расстояние между наноразмерными частицами;  $\alpha$  – угол наклона участка  $M_5M_6$  (процесс упрочнения покрытия за счет изменение размера зерен),  $\beta$  – угол наклона участка  $M_6M_7$  (процесс упрочнения покрытия за счет скопления дислокаций вокруг наночастицы);  $\sigma$  – длина элементарной «ячейки» (расстояние между структурами)



The scheme in Figure 2 represents dependence of microhardness on coordinate of every particular element. In the notation, we follow work [21]. Here,  $M_1(l_{m1}; h_m)$  is an arbitrary initial point for building the diagram, which characterizes microhardness of the basic coating material,  $M_2(l_{c1}; h_c)$  is the location at distance  $\Delta_1$  from  $M_1$ , where a greater microhardness was reached on account of grain fragmentation,  $M_3(l_{p1,2}; h_p)$  is the location of a nanoparticle at distance  $\Delta_2$  from  $M_2$  with the respective microhardness,  $M_4(l_{c2}; h_c)$  is the location at distance  $\Delta_2$  from  $M_3$  where the corresponding magnitude of microhardness due to grain fragmentation was reached,  $M_5(l_{m23}; h_m)$  is the location at distance  $2(\Delta_1 + \Delta_2)$  from  $M_1$  with microhardness of the basic coating material,  $M_6(l_{c3}; h_c)$ ,  $M_7(l_{p3,4}; h_p)$ ,  $M_8(l_{c4}; h_c)$ ,  $M_9(l_{m4}; h_m)$  are locations analogous to  $M_2$ ,  $M_3$ ,  $M_4$  and  $M_5$  with the structure spacing  $\sigma$ . Thus, locations  $M_i$  determine segment boundaries and are the nodes of the overall piecewise-linear function.

When characterising local microhardness of NGCs, we employ the following way of looking: every location with a certain generalised coordinate within the elementary “cell”  $[l_{m1}; l_{m23}]$  macroscopically infinitely re-produced along the coordinate axis possesses some microhardness defined according to Vickers. To impose the generalised coordinate system onto a 3D-crystal, one has to use a bijective mapping depending on and to be constructed for every particular crystal structure. Important is that the structure spacing  $l_{p-p}$  instantly affects angles  $\alpha$  (the slope of segment  $M_5M_6$  associated with coating hardening due to grain fragmentation) and  $\beta$  (that of  $M_6M_7$  representing coating hardening due to dislocation crowding around the nanoparticle) both influencing the ultimate hardness  $H_u$  which, generally speaking, in the framework of presented model appears to be a superposition of microhardnesses  $h_p$ ,  $h_c$  and  $h_m$  within the structure spacing  $\sigma = 2(\Delta_1 + \Delta_2)$ :

$$H_u = k_p h_p + k_c h_c + k_m h_m \quad (4)$$

where  $k_p$ ,  $k_c$  and  $k_m$  – some coefficients.

On the other hand, local microhardness as a function of generalized coordinate  $h = h(l)$  constitutes the essence of processes in Figure 2. Properties of function  $h(l)$  enable on to uncover the NGC hardening mechanism. Within partial segments in Figure 2, we have:

$$h = \begin{cases} h_m + (l - l_{m1}) \tan \alpha, & \text{if } l \in [l_{m1}; l_{c1}] \\ h_c + (l - l_{c1}) \tan \beta, & \text{if } l \in [l_{c1}; l_{p1,2}] \\ h_p - (l - l_{p1,2}) \tan \beta, & \text{if } l \in [l_{p1,2}; l_{c2}] \\ h_c - (l - l_{c2}) \tan \alpha, & \text{if } l \in [l_{c2}; l_{m2,3}] \end{cases} \quad (5)$$

where  $\tan \alpha = \frac{h_c - h_m}{l_{c1} - l_{m1}}$ ,  $\tan \beta = \frac{h_p - h_c}{l_{p1,2} - l_{c1}}$ .

A mean microhardness of each partial segment in the piecewise-linear model in Figure 2 is the arithmetic mean value of microhardnesses at segment boundaries. In a one-dimensional model employed here, the NGC ultimate hardness is the value averaged out over microhardnesses of all partial segments:

$$H_u = \frac{1}{l_{p1,2} - l_{m1}} \left[ \frac{1}{2} (h_m + h_c) (l_{c1} - l_{m1}) + \frac{1}{2} (h_c + h_p) (l_{p1,2} - l_{c1}) \right] = \frac{1}{2} \frac{h_m (l_{c1} - l_{m1}) + h_c (l_{p1,2} - l_{m1}) + h_p (l_{p1,2} - l_{c1})}{l_{p1,2} - l_{m1}} \quad (6)$$

We make here the two notes. Firstly, Equation (6) reproduces the superposition principle formulated in Eq. (4):  $k_p = \frac{1}{2} \frac{l_{p1,2} - l_{c1}}{l_{p1,2} - l_{m1}}$ ,  $k_c = \frac{1}{2}$ ,  $k_m = \frac{1}{2} \frac{l_{c1} - l_{m1}}{l_{p1,2} - l_{m1}}$ . Secondly, Equation (6) reproduces the Hall-Petch equation. Since this is the grain fragmentation which is responsible for preventing the plastic shear expansion, Equation (6) can be re-written in the form

$$H_u = 1/2 h_c + \frac{\frac{h_m}{\sqrt{2}} \sqrt{l_{c1} - l_{m1}} \sqrt{\frac{l_{c1} - l_{m1}}{l_{p1,2} - l_{m1}}} + \frac{h_p}{\sqrt{2}} \sqrt{l_{p1,2} - l_{c1}} \sqrt{\frac{l_{p1,2} - l_{c1}}{l_{p1,2} - l_{m1}}}}{\sqrt{2(l_{p1,2} - l_{m1})}} \quad (7a)$$



from where it follows that  $H_g = 1/2 h_c$ , grain size  $D = 2(l_{p1,2} - l_{m1})$  and coefficient  $k$  in Equation (3) has the following structure:

$$k = \frac{h_m}{\sqrt{2}} \sqrt{l_{c1} - l_{m1}} \sqrt{\frac{l_{c1} - l_{m1}}{l_{p1,2} - l_{m1}}} + \frac{h_p}{\sqrt{2}} \sqrt{l_{p1,2} - l_{c1}} \sqrt{\frac{l_{p1,2} - l_{c1}}{l_{p1,2} - l_{m1}}} \quad (7b)$$

i.e. (i)  $k$  is a superposition of smallest ( $h_m$ ) and biggest ( $h_p$ ) local microhardnesses of elements, taken with factors  $2^{-1/2}$  modified by lengths of the respective segments and by ratios of their lengths and the grain size (both in powers  $-1/2$  as well), and (ii) in this piecewise-linear model, coefficient  $k$  comprises the grain size  $D$  explicitly as Equation (7b) can be transformed to the form:

$$k = h_m \sqrt{l_{c1} - l_{m1}} \sqrt{\frac{l_{c1} - l_{m1}}{D}} + h_p \sqrt{l_{p1,2} - l_{c1}} \sqrt{\frac{l_{p1,2} - l_{c1}}{D}} \quad (7c)$$

Thus, expression (6) enables one to approximately prognosticate ultimate hardness of NGC depending on properties of nanoparticles, coating material and the grain size, should one be able to determine  $l_{m',c'p}$ .

*A non-linear model.* In real nanocomposite galvanic coatings, microhardness changes from one point to another non-linearly because of many reasons even within homogeneous phases. Therefore, Equation (6) can illustrate the situation just as a very rough approximation. An obvious demerit of the model in Figure 2 is that the derivatives in points  $l_{m2,3}$  and similar aren't zero although it should be  $h'(l_{m2,3} - 0) = h'(l_{m2,3} + 0) = 0$ . A more advanced model is related to the microhardness function in the form

$$h = h_m + (h_p - h_m) \sin^2 \left( \frac{l - l_{m1}}{\sigma} \pi + \pi n \right), n = 0, \pm 1, \pm 2 \dots \quad (8)$$

where  $l \in [l_{m1}; l_{m2,3}]$ . The corresponding model is presented in Figure 3 and free of the demerits mentioned above. It is continuously differentiable everywhere and has the same periodicity as that in Figure 2. The maxima have coordinates  $l_{p(n)} = \sigma \left( \frac{1}{2} + n \right) + l_{m1}$ , minima  $l_{m(n)} = \sigma n + l_{m1}$ .

The other particular locations are inflection points  $l_{f1}$  and  $l_{f2}$  in which the intensity of microhardness variation changes. Their coordinates are  $l_{f1,2(n)} = \sigma \left( \pm \frac{1}{4} + n \right) + l_{m1}$ , the microhardness in inflection points is equal to:

$$h(l_{f1,2(n)}) = \frac{3}{4} h_m + \frac{1}{4} h_p \quad (9)$$

Unlike the model in Figure 2, the ultimate hardness is to be represented now by an integral with the integrand  $h(l)$  in Equation (8) and with the same logics as Equation (6):

$$H_u = \frac{1}{l_p - l_{m1}} \int_{l_m}^{l_p} \left[ h_m + (h_p - h_m) \sin^2 \left( \frac{l - l_{m1}}{\sigma} \pi \right) \right] dl = \frac{1}{2} (h_m + h_p) \quad (10a)$$

By analogy with Equations (7), we can consider Equation (10a) in the context of the form of Hall-Petch equation (3). In this non-linear model, the value of  $h_c$  associated in the linear model with grain fragmentation is explicitly absent. Its role could play here the value of microhardness  $h(l_{f1,2})$  in inflection points in Equation (9). Following the logics of Equations (7), we can write now:

$$H_u = H_g + \frac{1}{8} (h_m + 3h_p) \quad (10b)$$

where for the grain hardness we have the following expression now:  $H_g = \frac{1}{2} h(l_{f1,2})$ . The second term in Equation (10b) is then to be associated with the grain-size factor:

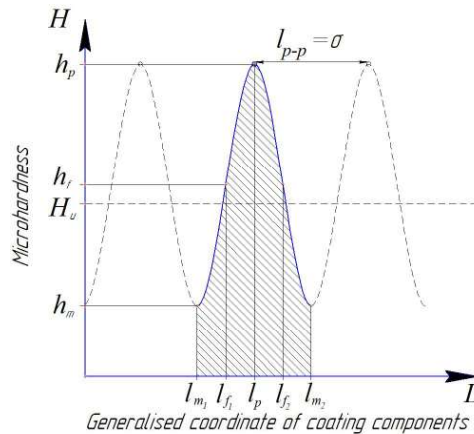
$$\frac{k}{\sqrt{D}} = \frac{1}{8} (h_m + 3h_p)$$



from where we obtain

$$k = \frac{1}{8} (h_m + 3h_p) \sqrt{D} = \frac{1}{4\sqrt{2}} (h_m + 3h_p) \sqrt{l_p - l_{m1}} \quad (10c)$$

As in the piecewise-linear model, coefficient  $k$  comprises the grain size  $D$  explicitly again.



**Figure 3 – Schematic presentation of a non-linear model of nanocomposite coating hardening.  $L$ -coordinate  $l_p$  corresponds to the maximum,  $l_{m1}$  and  $l_{m2}$  to the minima,  $l_{f1}$  and  $l_{f2}$  to the inflection points. For other notations s. Figure 2.**

**Рисунок 3 – Схема нелинейной физико-математической модели механизма упрочнения нанокomпозиционных покрытий.  $L$ -координата  $l_p$  соответствует максимуму,  $l_{m1}$  и  $l_{m2}$  – минимумам,  $l_{f1}$  и  $l_{f2}$  – точки перегиба. Для других обозначений см. Рисунок 2.**

**Results.** Before we apply the results of the previous section to some galvanic coating, we are to make some comments on the models above. The advantage of the piecewise-linear model is its clear structure that enables one to trace the features of the whole approach to understand its strengths and weaknesses. An upgrade of the piecewise-linear to a non-linear model of the nanocomposite galvanic coating hardening lets the latter not only inherit the principal structural features of the former but also obtain a more physically reasonable pattern. That the nonlinear model carries fewer parameters is one of its concomitant advantages while keeping in mind that some parameters of the piecewise-linear model are hard to determine and therefore to deal with.

One of the circumstances that may need to be commented on is the generalised coordinate introduced. It refers to those parameters that describe the system configuration essential in the sense of its hardening properties. Unlike analytical mechanics, these parameters may not uniquely define the system configuration in the sense of geometrical positions in a 3D-space but our goal in a physical description of the problem is different and related to hardening issues rather than to dimensionally precise geometrical locations of system elements. The two structural elements depicted in Figure 1 (from  $l_{m1}$  to  $l_{m23}$  and from  $l_{m23}$  to  $l_{m4}$ ) can always be considered as positioned along some axis. Added as neighbouring to the second element, the third element can further be considered as positioned along another axis piercing both the second and the third elements, but this axis is generally expected to intersect the first axis at some non-zero polar and azimuth angles. One can think of this generalised coordinate as a serpentine-like ribbon piercing the coating through.

Another feature of the piecewise-linear model is the coating microhardness linearity influenced by microhardnesses of elements within particular segments what was referred to above. In real coatings, such a linearization is expected to be justified under particular conditions which probably include temperate gradients of microhardness within the coating and its elements. This temperance is to be conditioned through the coating relevant internal structure (dislocations and grain fragmentation). The piecewise-linear model contains a number of generalized coordinate parameters which are physically transparent but not always easy to determine. Therefore, this model is to be considered here as a bridge for more advanced non-linear model which inherits all topological features of the piecewise-linear model.

Both models enable one to reduce final expressions (6) and (10a) the form resembling the Hall-Petch equation (3). This may be perceived as questionable in the case of the piecewise-linear model because of a rather big number of parameters but looks much more transparent in the case of the non-linear model.





Reduction to the Hall-Petch equation is actually no end in itself, the more so because this equation isn't the absolute truth in all the cases [8].

According to the non-linear model (Equation (10)), we calculated hardness of the Cr-based coating. For calculations, we used our own data [24] (s. also Table C1) for microhardness of the base coating material (chromium)  $h_m = 9.6$  hPa, grain size  $D = 7.2 \cdot 10^{-5}$  cm. Microhardness of nanoparticles ( $Al_2O_3$ , AlN, SiC, TiC, WC,  $K_2O \cdot nTiO_2$ )  $h_p = 20$  hPa [1, 5, 8]. According to Equation (10a), the ultimate hardness appeared to constitute 14.80 hPa. Compared to the hardness value 14.32 hPa determined in experiments [8], this seems to be rather acceptable match as the relative error constitutes 3.35%. Upon reduction to the Hall-Petch equation, the Hall-Petch constants appeared to be calculated and constituted  $H_g = 6.1$  hPa and  $k = 7.38 \cdot 10^{-3}$  hPa·m<sup>1/2</sup>.

**Conclusions.** The paper presents the one-dimensional superposition model to calculate ultimate hardness of nanocomposite galvanic coatings based on the data for [micro-]hardnesses of the base material and nanoparticles as well as mean grain size. The model involves the generalized spatial coordinate adjusted to take into account structural peculiarities of the coating and crystal (grain) periodicity. The final equation for ultimate microhardness has a very simple compact form

$$H_u = \frac{1}{2}(h_m + h_p)$$

where  $h_p$  and  $h_m$  are microhardnesses of the base coating material and of nanoparticles respectively, and appears to be reducible to the Hall-Petch equation form and applicable to calculations of ultimate hardness of nanocomposite galvanic coatings. Sample calculation for chromium-based nano-composite coating resulted in a relative error of 3.35% compared to the hardness magnitude obtained in experiments. The use of this simple approach enables one to make easy estimates related to nano-composite coatings aimed, e.g., to reduce wear in friction pairs et cetera.

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