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BRIEF COMMUNICATIONS

Synergistic Effect in Nickel–Teflon Composite Electrolytic Coatings

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Abstract—The possible synergistic effect in the manifestation of the wear resistance and antifriction properties of nickel–Teflon composite electrolytic coatings was analyzed. The results of calculations of the diagnostic properties of the coatings in terms of the "concentration-wave" model are discussed in comparison with the corresponding experimental data.

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It is well known [1] that nickel–boron–Teflon composite electrolytic coatings (CECs) exhibit a synergistic effect: Their wear resistance and antifriction properties are better than those calculated in terms of the additive model. The synergism of the solid and lubricating components consists in that the lubricating Teflon phase is concentrated on the friction surface, thus enhancing the antifriction characteristics and wear resistance of the solid phases of the coatings, and that the coatings contain nanoparticles of certain solid phases (probably borides Ni_3B and Ni_2B). These nanoparticles have a spherical or cylindrical shape with a cross section diameter of 1.2–2.5 nm; they apparently exhibit the properties of solid lubricants [1].

To verify the assumption that nanoparticles of only low-boron nickel phases contribute to the overall synergistic effect observed with nickel–boron–Teflon CECs, we examined boron-free nickel–Teflon CECs. In this case, the possible synergism would be exclusively due to the first factor, concentration of Teflon microparticles on the friction surface.

The calculated data for the linear wear I^0_{lin} and friction coefficient f^0 of nickel–Teflon CECs in the CEC/CEC friction couple were obtained within the two-component approximation of the "concentration-wave" model [2] by the formulas:

$$I^0_{\mathrm{lin}} = \alpha\langle I^0_{\mathrm{lin,\,solid}}\rangle + (1-\alpha)\langle I^0_{\mathrm{lin,\,lub}}\rangle + \delta(\langle I^0_{\mathrm{lin,\,solid}}\rangle - \langle I^0_{\mathrm{lin,\,lub}}\rangle), \quad (1)$$

$$f^0 = \alpha\langle f^0_{\mathrm{solid}}\rangle + (1-\alpha)\langle f^0_{\mathrm{lub}}\rangle - \delta(\langle f^0_{\mathrm{solid}}\rangle - \langle f^0_{\mathrm{lub}}\rangle), \quad (2)$$

where $\alpha = \alpha_{\mathrm{solid}}$ and $(1-\alpha) = \alpha_{\mathrm{lub}}$ are the volume fractions of the solid and lubricating components of CEC, respectively; $\delta = 4(1-\alpha)\alpha^2[1 - k(1-k_{\mathrm{n}})]$, relative synergistic effect; k, size parameter characterizing the dispersity of the solid component of CEC: the ratio between the mean size of microparticles r_{solid} of solid phases in the surface later and the thickness of this layer Δx, i.e., $k = r_{\mathrm{solid}}(r_{\mathrm{solid}} + \Delta x)^{-1}$ (at $r_{\mathrm{solid}} \to \Delta x$ $k \to 0.5$); k_{n}, nanostructure parameter of the solid component of CEC: the volume fraction of solid phase nanoparticles of spherical or cylindrical shape in the surface layer Δx ($0 \le k_{\mathrm{n}} < 1$); $\langle I^0_{\mathrm{lin,\,solid}}\rangle$, $\langle f^0_{\mathrm{solid}}\rangle$, $\langle I^0_{\mathrm{lin,\,lub}}\rangle$, and $\langle f^0_{\mathrm{lub}}\rangle$ are the mean values of the corresponding individual characteristics in the solid and lubricating components of CEC [2].

In accordance with the data of Kryachko et al. [3], the influence of the characteristics of counterbody (CB) material (St45 steel in our case) on the CEC properties was taken into account as follows:

$$I_{\mathrm{lin}} = I^0 + (\Delta\alpha - \Delta\delta)(I^0_{\mathrm{solid}} - I^0_{\mathrm{lub}}) + (\alpha + \delta)(I_{\mathrm{CB}} - I^0_{\mathrm{solid}}), \quad (3)$$

$$f = f^0 + (\Delta\alpha - \Delta\delta)(f^0_{\mathrm{solid}} - f^0_{\mathrm{lub}}) + (\alpha + \delta)(f_{\mathrm{CB}} - f^0_{\mathrm{solid}}), \quad (4)$$

where $\Delta\delta \cong 2\alpha(3\alpha - 2)\Delta\alpha$ is the change in the relative synergistic effect [3]; $\Delta\alpha = \alpha^* \cong (\alpha I^0_{\mathrm{solid}} + I_{\mathrm{CB}})\times$

Table 1. Phase composition and concentration of components of composite coatings

Coating	CEC component	Phase composition	Weight fraction	Volume fraction	α
			%		
Ni	Solid	Ni	100	100	1.00
	Lubricating	–	0	0	
Ni–Teflon	Solid	Ni	99.1	95.4	0.954
	Lubricating	Teflon	0.9	4.6	
	Solid	Ni	98.3	91.6	0.916
	Lubricating	Teflon	1.7	8.4	
	Solid	Ni	96.9	85.6	0.856
	Lubricating	Teflon	3.1	14.4	

$(I^0_{solid} + I_{CB})^{-1} - \alpha = (1 - \alpha)I_{CB}(I^0_{solid} + I_{CB})^{-1}$ is the change in the volume concentration of solid phases in going from CEC to wear products of the CEC/CB couple (for the CEC/CEC friction couple, $\Delta\alpha$ is formally equal to zero) [3]; $(\alpha + \delta) = \alpha[1 + 2\alpha(1 - \alpha)(1 + k_n)]$; I^0_{lin} and f^0 are the linear wear rate and CEC friction coefficient in the CEC/CEC friction couple, determined by formulas (1) and (2).

Composite electrolytic coatings with Teflon volume fractions of 4.6, 8.4, and 14.4% were prepared from an electrolyte of the following composition ($g\,l^{-1}$): nickel chloride hexahydrate 200–250, nickel sulfate heptahydrate 2.5–5.0, boric acid 25–40, Chloramine B 0.5–2.5, and F-4D-E (Teflon) emulsion 10–20. Electrolysis conditions: pH 1.0–5.5, temperature 18–30°C, cathode current density 0.5–9 $A\,dm^{-2}$.

From the data on the phase composition and concentration of CEC components (Table 1), using the calculation procedures described in [2, 3], we obtained the concentration dependences $I_{lin}(\alpha)$ and $f(\alpha)$ at fixed values of the parameter k_n = 0, 0.05, 0.1, 0.15, and 0.2 for the CEC/CEC and CEC/St45 friction couples.

Note that the individual characteristics of the solid and lubricating CEC components that we used in the calculations, namely, for nickel, $I_{lin,\,solid} = 1.1\ \mu m\,h^{-1}$, $f_{solid} = 0.25$; for Teflon, $I_{lin,\,lub} = 7.5\ \mu m\,h^{-1}$, $f_{lub} = 0.03$; and for St45 steel, $I_{lin,\,St45} = 1.2\ \mu m\,h^{-1}$, $f_{St45} = 0.24$, corresponded to the stationary step of the mode of dry friction of two identical materials at a specific load of 3 MPa and a friction velocity $V = 0.048\ m\,s^{-1}$.

Analysis of the $I_{lin}(\alpha)$ dependences for CEP in the case of friction over the identical material showed that the minimum of the linear wear rate, 0.673 $\mu m\,h^{-1}$, at $k_n = 0$ is attained at $\alpha = 0.86$. As the nanostructure parameter increases to 0.20, the minimum of the linear wear rate decreases to 0.401 $\mu m\,h^{-1}$ at $\alpha = 0.83$. In the case of friction over St45 steel, $(I_{lin})_{min} = 0.520\ \mu m\,h^{-1}$ for $k_n = 0$ is attained at $\alpha = 0.80$, and with an increase in k_n to 0.20, this value decreases to 0.356 at $\alpha = 0.75$. Apparently, the observed quantitative changes in $I_{lin}(\alpha)$ dependences are due to a rise in the contribution of nickel nanoparticles to the synergistic effect of the CECs.

An analysis of the $f(\alpha)$ dependences revealed a regular decrease in the friction coefficient with an increase in the volume fraction of Teflon and decrease in f_{CB} in the entire range of α. However, the maximal synergistic effect, i.e., the maximal deviation of the dependences $f(\alpha)$ from the values calculated in terms of the corresponding additive model, is attained at $\alpha = 0.72 \pm 0.02$.

It should be noted that the calculated data can be used for determining the compositions of Ni–Teflon CECs with prescribed wear resistance and antifriction properties. From the same data, we can determine the optimal composition of a wear-resistant antifriction coating, i.e., a formulation with the minimal value of $(I_{lin} f)|k_n$. For example, at $k_n = 0$, the minimal value of this parameter is attained for CECs (friction over St45 steel) at the Teflon volume fraction of about 0.25.

Experimental data on the wear resistance of CECs in friction couples with St45 steel are in reasonable agreement with the calculated data at $k = 0.5$ and $k_n = 0.07$ (Table 2). The nanostructure parameter equal to 0.07 was used for obtaining predictable data on the other tribological characteristics of the CECs (Table 2).

Thus, the concentration-wave model with the parameters $k = 0.5$ and $k_n = 0.07$ allows satisfactory interpretation of the experimental data on the linear wear rate of Ni–Teflon CECs in friction over St45 steel and prediction of the corresponding friction coefficients. Within the framework of the model we used, the quantity $k_n > 0$ means not only a high dispersity of micro-

Table 2. Wear and antifriction properties of nickel and composite coatings in a friction couple with St45 steel

Coating	α	Linear wear rate I_{lin}, μm h^{-1}		Friction coefficient f	
		calculation	experiment	calculation	experiment
Ni	1.000	1.20	1.20	0.24	0.24
Ni–Teflon	0.954	0.782	0.79	0.217	–
	0.916	0.608	0.59	0.192	–
	0.856	0.455	0.46	0.156	–
Ni–B	1.000	1.100	1.10	0.25	0.25
Ni–B–Teflon	0.954	0.767	0.74	0.218	0.21
	0.898	0.630	0.56	0.185	0.17
	0.835	0.434	0.42	0.155	0.15

particles of Ni and γ-Fe phases, but also the presence among them of spherical or cylindrical nanofragments enhancing the effect of the CEC lubricating component.

It should be noted that the experimental data on the linear wear rate and friction coefficient for the nickel–boron–Teflon CEC, reported in [1] (Table 2), were satisfactorily described by the concentration wave model with a higher nanostructure parameter $k_n = 0.17$. In so doing, it was assumed [1] that, along with Teflon concentration on the surface of the CEC/St45 friction couple, nanoparticles of the specific shape were formed only from boron-containing phases.

The data we obtained suggest that, in nickel–boron–Teflon CECs, not only Ni_3B and Ni_2B, but also Ni and γ-Fe phases act in friction as lubricating components along with Teflon. On the whole, the role of boron-containing phases consists in that the wear resistance of the coatings is enhanced owing to their individual charactetistics I^0_{lin} and the friction coefficient of the surface decreases owing to the formation of the corresponding nanoparticles.

CONCLUSIONS

(1) Ni–Teflon composite electrolytic coatings show a synergistic effect consisting in enhancement of their wear resistance and antifriction properties, compared to the additive values.

(2) The synergism of the solid and lubricating components of the composite electrolytic coatings under consideration consists in concentration of Teflon on the wear surface, enhancing the antifriction properties and wear resistance of nickel, and in the presence of spherical or cylindrical nickel nanoparticles acting as solid lubricants.

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