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LETTERS
TO THE EDITOR

Synergetic Change of Tribochemical Properties of Copper in the Presence of Quaternary Ammonium Compounds at the Surface

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It has been earlier demonstrated that sequential chemisorption of triamon and alkamon (the formulations based on quaternary ammonium compounds with C_1–C_2 and C_{16}–C_{18} substituents at the nitrogen atom, respectively) at dispersed aluminum leads to the synergetic increase of the high-temperature metal oxidation by at least 45% [1, 2]. The adsorption of surfactants with varied length of the alkyl chain is of interest in view of adjustment of the solid surface reactivity as well as the effect on the water-repellent and antifriction properties of the modified metal [2–5]. The interest towards study of the effect of triamon and alkamon adsorption on copper tribochemical properties has been directed by the two following major reasons. Firstly, the surface of copper powders is generally "cleaner" than that of Al samples, capable of heteroatomic interaction with quaternary ammonium compounds [2]. Secondly, the systems containing copper and lubricant have exhibited the non-wear Kragelsky–Garkunov effect resulting in decrease of the friction coefficient by an order of magnitude [4].

The XPS studies conducted in this work demonstrated that sequential chemisorption of triamon and alkamon at the dispersed copper resulted in enhancement of the metal–nitrogen interaction in the surface layer. The water-repellent properties of the metal were improved, and addition of the modified metal to the lubricant of the tribology pair led to synergetic decrease of the integral friction coefficient (the friction force) at least four times.

The PM-1 grade copper powder (GOST 4960-75) with the specific surface area of 0.34±0.02 m^2/g was treated with triamon and(or) alkamon vapor at room temperature as described in [2, 6]. The content of the major component of the mentioned ammonium compounds was >95 wt % in the liquid phase (TU 2482-030-05744685-2003 and GOST 10106-75) and >99.5 wt % in the vapor. The water-repellent properties of the specimens were determined from the water vapor adsorption as measured by the gravimetric dessicator method at the relative pressure of p/p_0 = 0.98±0.02. The integral friction coefficient D (proportional to the friction force in the steel–steel tribology pair with the lubricant) was determined via the acoustic emission method using the ARP-11 certified instrument at 20–300 kHz according to the procedure described in GOST 27655-88. The I-20 oil was used as the grease, the (modified) copper powder was introduced into the oil, the copper content being equal in all the experiment.

According to the EDX spectroscopy data (an EDAX/TSL analytical attachment, recording at 6 kV), the untreated copper powder did not contain any noticeable amounts of nitrogen or sulfur, the content of other elements was as follows: copper at least 91.6 mol %, oxygen 3.1 mol %, and carbon 4.7 mol %. After treatment in alkamon vapor, the copper sample with the specific surface area of 0.35 m^2/g contained 0.2 mol % of nitrogen, 0.3 mol % of sulfur, 3.7 mol % of oxygen, and 5.8 mol % of carbon. The relative mass increase due to water vapor adsorption at the Cu–alkamon material was a_1 0= .0299, significantly lower than that in the case of initial copper (a = 0.0445). The similarly prepared Cu–triamon sample with specific surface area of 0.32 m^2/g contained 0.4 mol % of nitrogen, 0.4 mol % of sulfur, 3.7 mol % of oxygen, and 5.0 mol % of carbon; the water vapor adsorption was a_2 = 0.0268. The Cu–triamon–alkamon material (prepared via sequential treatment in the triamon and alkamon vapors) with the specific surface area of 0.36 m^2/g contained 0.7 mol % of nitrogen, 0.8 mol % of sulfur, 3.1 mol % of oxygen, and 6.3 mol % of carbon; the water vapor adsorption was a_3 = 0.0260 [5].

Measurement of the integral friction coefficient of the test system with the addition of the copper powders at the loading pressure of 40 MPa gave the following results: D_1 = 1300 (Cu-alkamon), D_2 = 1100 (Cu–triamon), D_3 = 270 (Cu–triamon–alkamon) [5], D = 1580 (initial copper), and D_0 = 1690±50 (no copper additive). Hence, copper modification resulted in the decreased friction in the test system. Comparison of the corresponding D values demonstrated that the sequential treatment with both modifiers was 4–5 times more efficient than that of the individual components. Hence, the decrease in the D value due to copper modification with alkamon and triamon was evidently synergetic in nature.

Interestingly, the somewhat weaker synergetic effect was observed as far as water vapor adsorption was considered: comparison of the a_1, a_2, and a_3 values revealed that the sample obtained via sequential treatment with the both modifiers exhibited the lowest a value. Interestingly, the copper sample treated with the low-molecular triamon showed lower adsorption of water as compared with the case of modification with alkamon. That was likely due to the horizontal orientation of the organic substituents at the Cu–triamon sample surface and to the better stabilization of the smaller triamon molecules at the metal surface; both factors prevented interaction of water molecules with hydrophilic sites at the copper surface [7].

The XPS data evidenced that the strongest Cu←N electronic interaction between the metal and the adsorbed ammonium molecules occurred in the case of the Cu–triamon–alkamon sample. The determined bond energies of the electrons of the characteristic levels were as follows: E_b(Cu2p) = 932.8 eV and E_b(N1s) = 404.0 eV (Cu–alkamon–triamon); E_b(Cu2p) = 933.5 eV and E_b(N1s) = 402.1 eV (Cu–alkamon); E_b(Cu2p) = 933.2 eV and E_b(N1s) = 402.5 eV (Cu–triamon); and E_b(Cu2p) = 933.8 eV (initial copper). The spectra were excited with AlK_α radiation (1486.6 eV), the analyzer chamber pressure during the recording was below 1.3 mPa. Stability of the surfactants adsorbed at the copper surface in the course of the spectra recording was confirmed by the constant pressure in the analyzer chamber and the intensity of the characteristic N1s peak in the spectra during the experiment. The spectra were obtained using an Escalab 220 iXL instrument (Leipzig University).

The synergetic change of the tribochemical properties of the studied systems could at the first approximation be due to the strengthening of the adhesion between copper and the surfactants, other conditions (the loading pressure, the dispersion state, and the additive content) being the same. Under the harsh conditions of the tribology test (p = 40 MPa, close to the dry friction conditions [4]), the I-20 oil was pushed out the friction pair contact zone [6]. The friction was then to a large extent determined by the antifriction effect of the solid additive. According to the commonly accepted views, the highest antifriction and the protective properties of the surfactant film at the solid surface are attained in the case of the film hydrophobicity and its good adhesion to the solid support [3, 4]. The results of this work coincided with these fundamental views and underscored the importance of the adhesion factor [2, 6, 7]. The reasons for the increased bond energy of the N1s level in the metal–triamon–alkamon samples have been earlier discussed in [1].

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