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Water repellent properties of dispersed metals containing low-dimensional forms of ammonium compounds on the surface

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Abstract. For the first time the change of the water repellent properties of dispersed copper, modified using quaternary ammonium compounds on 24 h time scale in saturated water vapours was studied. Exponential time dependences of the water repellent properties of dispersed copper with adsorbed QAC were derived and characterized. It was established that the samples modified in mixed and consistent modes by both modifiers reach the saturation state faster than others, due to the small number of hydrophilic centers on the surface of metals. The last conclusion was confirmed by the distribution spectra of centers of adsorption, which were obtained by the adsorption of acid-base indicators for more dispersed samples based on aluminum powder.

1. Introduction

Dispersed metals are widely used in various fields of science and technology, including electronics, tribotechnology and heterogeneous catalysis. Due to the high chemical activity of the particles, dispersed metals can be oxidized in air, primarily by water vapours. Therefore, to stabilize the functional properties of solid materials containing dispersed metals, it is important to create the protective films on the surface of particles of such metals to improve their water repellent properties. One of the promising methods is layering of different-sized molecules of quaternary ammonium compounds (QAC). The advantages of the method are the possibility of applying submonomolecular coatings, low vapor pressure of QAC, gas-phase modification at room temperature, and environmental friendliness of the method [1–3].

Previously, it was shown that the chemisorption of QAC-based cationic surfactants has a positive effect on water repellent and antifriction properties of metals, such as aluminum [2, 3]. However, there are more interesting objects for modification such as dispersed copper powders, not only from the point of view of surface chemistry, but also in case of variety of practical use.

In this research, the water repellent properties of dispersed copper with adsorbed QAC on the surface were studied in saturated water vapours (5–24 h). This topic is significant not only for regulation of different properties of surface of dispersed metals, but also for establishment of quantitative regularities between synthesis, composition, structure and properties of various heterogeneous materials, containing nanostructured metals, which is a basic goal of modern physics and chemistry of low-dimensional systems.



2. Materials and methods

Copper powder PM-1 (GOST 4960-75) with specific surface area of $0.34 \pm 0.02 \text{ m}^2/\text{g}$ and with specific volume of monolayer of nitrogen of 0.08 ml/g was chosen as the initial sample of dispersed metal. More dispersed non-porous aluminum powder PAP-2 was also used to analyze the distribution spectra of adsorption centers on the surface of metal samples. According to electron microscopy, the modification of the surface of metals does not lead to a significant change of the shape and size of the particles.

Metal powders were treated in vapours of alkamon (A), triamon (T) and hydrophobic silicone-organic liquid (HSL-94) at room temperature using various adsorption programs. The composition of the obtained samples with adsorbed ammonium or silicon-organic compounds was determined by EDX spectroscopy (analytical attachment EDAX/TSL, shooting mode – 6 kV). The binding energies of the electrons of chemical elements on the surface were determined by the X-ray photoelectron spectroscopy. Measurements of the X-ray photoelectron spectra were carried out on Escalab 220iXL (University of Leipzig). The binding energy of the characteristic level was determined with accuracy of 0.1 eV. The water repellent properties of the samples were evaluated by parameter $1/a$, which was calculated from the value of adsorption of water vapours (a). Adsorption of water vapours was measured gravimetrically (g/g) at relative vapour pressure of $p/p_0 = 0.98 \pm 0.02$ and temperature of $20 \pm 2 \text{ }^\circ\text{C}$. The fact of adsorption of water vapours on metal was proved by the presence of the O 1s peak with binding energy of 532.5 eV in the X-ray photoelectron spectra of samples [4]. The mathematical description of the process was obtained using programs such as MathCad and MS Excel.

Alkamon and triamon are widespread surfactants based on quaternary ammonium compounds with the general formula of $[\text{R}_1\text{R}_2\text{R}_3\text{R}_4\text{N}^+]\text{X}^-$, where $\text{R}_1, \text{R}_2, \text{R}_3, \text{R}_4$ – organic radicals on a nitrogen atom; X^- – is a polar group, usually an inorganic anion. It should be noted that alkamon has larger organic radicals ($\text{C}_{16}\text{--}\text{C}_{18}$) than triamon (C_1, C_2). The composition of technical triamon correspond to the formula: tris- (β -oxyethyl) methyl ammonium methyl sulfate $[(\text{HOC}_2\text{H}_4)_3\text{N}^+\text{CH}_3][\text{CH}_3\text{SO}_4^-]$. The industrial hydrophobizator HSL-94, which was used in the research, in fact, was a reference model.

3. Results and discussion

Modification of samples of dispersed copper was carried out according to the methods [2, 3, 5] and confirmed by EDX-spectroscopy. Due to the fact that the initial Cu powder did not contain any noticeable amount of nitrogen and sulfur, it can be assumed that their presence in modified powder is a result of chemisorption of QAC. Therefore the fact of chemisorption can be proved by the chemical composition of the samples. The content in initial powder is: copper at least 91.6 at. %, oxygen is 3.1 at. %, and carbon is 4.7 at. %. After treatment in alkamon vapours, the copper sample with the specific surface area of $0.35 \text{ m}^2/\text{g}$ contained 0.2 at. % of nitrogen, 0.3 at. % of sulfur, 3.7 at. % of oxygen and 5.8 at. % of carbon. The similarly prepared Cu/A (treated in triamon vapours) sample with specific surface area of $0.32 \text{ m}^2/\text{g}$ contained 0.4 at. % of nitrogen, 0.4 at. % of sulfur, 3.7 at. % of oxygen and 5.0 at. % of carbon. The Cu/T/A sample (prepared via sequential treatment in the triamon and alkamon vapours) with the specific surface area of $0.36 \text{ m}^2/\text{g}$ contained 0.7 at. % of nitrogen, 0.8 at. % of sulfur, 3.1 at. % of oxygen and 6.3 at. % carbon [5].

Based on the experiments of adsorption of water vapors by various samples, the parameter a (value of adsorption of water vapours) was converted into parameter $1/a$, which characterizes the water repellent properties of the samples (table 1).

The kinetic equation of mass transfer (1) for adsorption processes was used as the basis to describe the process of adsorption of water vapor on metal in time [6, 7], where $n(t)$ – is the function of the amount of adsorbed water; k – is the kinetic coefficient of adsorption; t – is the time

$$\frac{dn(t)}{dt} = -k \times n(t) \Rightarrow n(t) \sim e^{-kt}, \text{ where } n(t) \sim a. \quad (1)$$

After elementary mathematical transformations

$$1/a \sim 1/n(t) \sim e^{kt}. \quad (2)$$

Table 1. Examples of conversion of value of adsorption a into parameter $1/a$.

Sample	Exposure time, h							
	3		6		12		24	
	a , rel. un.	$1/a$	a , rel. un.	$1/a$	a , rel. un.	$1/a$	a , rel. un.	$1/a$
Cu-initial	0.00437	229	0.00438	229	0.00655	153	0.00657	153
Cu/A+T	0.00197	509	0.00295	339	0.00393	255	0.00394	255
Cu/A	0.00598	167	0.00498	201	0.00497	201	0.00499	201
Cu/T	0.00401	250	0.00404	250	0.00501	200	0.00509	200
Cu/T/A	0.00399	251	0.00499	201	0.00598	167	0.00599	167
Cu/HSL	0.00293	341	0.00294	341	0.00391	256	0.00488	205

The correlation dependencies, based on the experimental data were plotted in the MathCad (figure 1). The part of the graph, which is parallel to the OX axis (time) corresponds to the stage of saturation of the sorbent. A mathematical description of the function $1/a = f(t)$ with sufficiently high coefficient of determination R^2 (table 2) was obtained.

Table 2. Approximated equations $1/a = f(t)$ and coefficient of determination R^2 .

Sample	Equation $1/a = f(t)$	Coefficient of determination R^2
Cu-initial	$f(t) = 104 + 201e^{-0.126t}$	0.838
Cu/(A+T)	$f(t) = 241 + 543e^{-0.229t}$	0.982
Cu/T/A	$f(t) = 166 + 217e^{-0.31t}$	0.997
Cu/T	$f(t) = 191 + 95e^{-0.126t}$	0.838

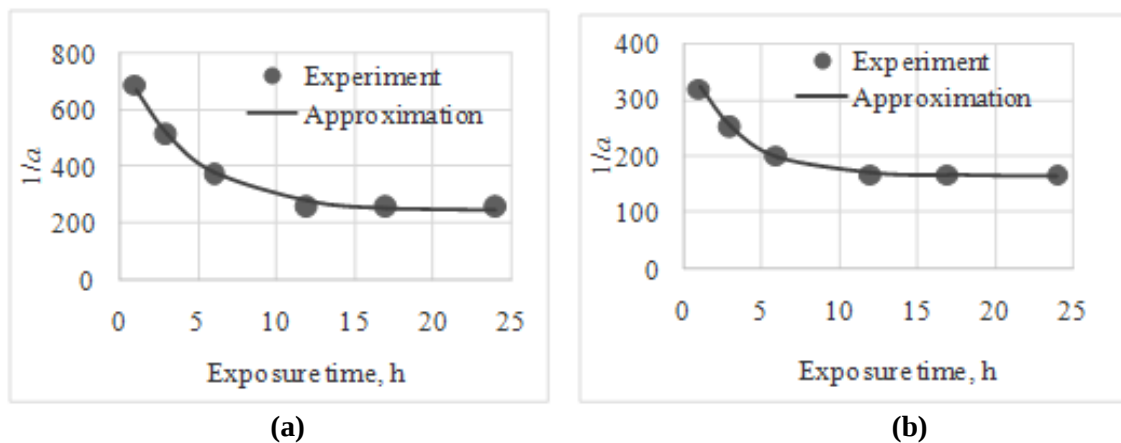


Figure 1. Dependency graphs $1/a = f(t)$ for Cu/A+T (a) and Cu/T/A (b) samples.

The shape of the curves of the dependences and equations are similar to relaxation curves for other types of hydrophobic adsorbents, which were studied in Institute of general physics in Moscow [7]. In our previous researches of dispersed aluminum, where the exposure time was significantly greater (more than 320 h), the dependences of water repellent properties were approximated using a set of elementary functions ($\ln t$, t^2 and Gaussian function) [8].

The sample Cu/(A+T) after 24 h of interaction with saturated water vapor remains the most hydrophobic (the maximum values are $1/a$ (table 1)). According to figure 1 and table 2 samples treated

with T and A in mixed and sequential modes (the maximum value of the coefficient k), reach the saturation state of the surface faster than the original copper or the sample treated with only one modifier (T).

It is possible to trace the change in the nature of the active centers on the surface of metal powders during the layering of A and T by plotting the distribution curves of the adsorption centers. The curves can be plotted by adsorption of acid-base organic indicators with constant of ionization (acid force pK_a) from -0.3 to 14.2 [9, 10]. The most informative and relief spectra of the distribution of adsorption centers were obtained for aluminum powder (PAP-2), its specific surface ($2.6 \pm 0.1 \text{ m}^2/\text{g}$) almost 8 times greater than the specific surface area of copper powder.

According to figure 2 mixed chemisorption of A and T on the metal leads to the decrease of the number of Lewis acid centers ($pK_a = 14.2$) by an order, in comparison with the original aluminum powder. These centers correspond to the vacant orbitals of the Al atom, which can accept an electron pair, including the donor-acceptor interaction of QAC with a metal [2, 9, 10]. In addition, the intensity of the peaks, which are responsible for the hydrate-hydroxyl coating decreases for $pK_a = 5$ and $pK_a = 9.5$. This fact, confirms the thesis of reducing of the number of hydrophilic centers in case of mixed treatment with A and T. In case of layering of T or A separately, as seen from figure 2, the effects of the hydrophobization of the surface and the screening of electron-acceptor centers on the metal (the pK_a range around 14), are weaker.

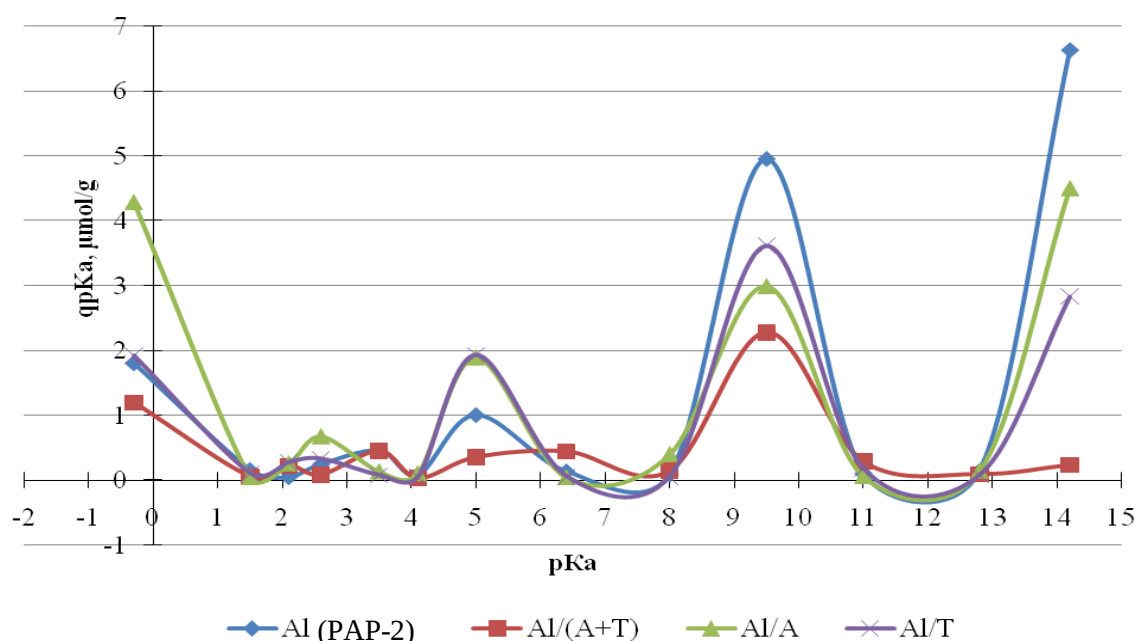


Figure 2. Distribution of acid-base centers on the surface of modified Al-powders.

4. Conclusion

For the first time the change of the water repellent properties of dispersed copper, modified using quaternary ammonium compounds (QAC) on 24 h time scale in saturated water vapours was studied.

Sufficiently accurate time exponential dependences of the water repellent properties of dispersed copper treated with QAC were derived and characterized. It was established that the samples, prepared by chemisorption of both modifiers in mixed and consistent regimes, reach the saturation state on the curves ($1/a - \text{time}$) faster than others, due to the small number of hydrophilic centers on the surface of metals. The last conclusion was confirmed for similarly modified Al-powders by the effect of halving of the intensity of the peaks ($pK_a = 5$ and $pK_a = 9.5$) in the distribution spectras of the adsorption centers of acid-base organic indicators.

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