Stabilization of disperse metals by nitrogen-containing tensides with different-sized molecules

A G Syrkov, V V Taraban, V R Kabirov and M O Silivanov

Department of general and technical physics, Saint Petersburg Mining University, 199106, Saint Petersburg, Russia

E-mail: syrkovandrey@mail.ru

Abstract. The samples based on disperse aluminum and copper with similar hydrophobic films on the surface were analyzed and compared. It was established that sorption of water vapor by copper sample decreases by 1.5 times in 145 hours, as a result of sequential layering of ammonium compounds with different-sized hydrocarbon radicals on the nitrogen atom (C\(_{1,2}\) and C\(_{17}\)). Sequential layering of ammonium compound with large C\(_{17}\) – radical and organohydride siloxane on copper leads to the decrease of water vapor adsorption by 3 times. The common pattern for Al and Cu samples modification is that the application of two-component layers of structurally similar components favors the formation of samples, stable to oxidizing effect of water.

1. Introduction

The hydrophobization of the disperse metals allows to stabilize the specific surface area during storage and exploitation. Moreover, the layering of special modification agents slows down the corrosion processes. Disperse metals are used in various technical and chemical processes (alloying, catalysis), as fillers for organopolymer compositions, as well as in electronics and other fields [1, 2]. Special properties are required for the metals, both in structure and composition of surface, and in their stability when interacting with humid air atmosphere and/or with aggressive substances in industrial conditions [1–3]. Thus, the study of the properties of the dispersed metals under various external influences, especially extreme ones, and the problems of stabilization of sorption properties in the high humidity air environment are important not only for basic science, but also for specific industry applications.

In this research, the features of formation of water vapor stable tensides nanofilms on metal were studied.

Tensides based on quaternary ammonium compounds (QAC) were applied to the metal surface according to method of layering of different-sized QAC and organosilicon compounds molecules, which is a promising way for regulating of hydrophilic-lipophilic and antifriction surface properties [2, 4, 5]. Disperse materials with the sufficiently hydrophobic surface with organophilic properties are obtained in certain modes of modification of the initial metal powder (Al, Cu, Ni, etc.). These materials are successfully used as part of the various oligomeric compositions (lubricants, paints, enamels), enhancing the functional properties [4, 6].

It was previously shown that the Gaussian function allows to achieve high accuracy of approximation of complex non-monotonic time dependence of water vapor sorption (a) or parameter 1/a (degree of surface hydrophobization) for modified samples of dispersed aluminum [6].
2. Materials and methods

Copper stabilized powder PMS-1 (GOST 4960-2009) was used as an initial disperse metal. The primary particle size is less than 80 μm (90%) and about 50 % of the particles is less than 43 μm; moisture content is less than 0.05%. Measurement of the particle size, particle distribution and calculation of the specific surface of samples were carried out on the basis of laser diffraction data (Malvern Mastersizer 3000). The mentioned material (figure 1) was chosen due to wide industrial usage and to the presence of hydrophobic stabilizer surface film based on sodium oleate, applied in the industrial conditions. The specific interest is driven by the possibility of synergistic enhancement of water-repellent properties by adsorption of QAC molecules on the surface.

Gas phase surface modification of copper powders was carried out in vapor of QAC-based surfactants alcamon (GOST 10106-75) and (or) triamon (TU 6-14-1059-83), as well as in vapor of hydrophobic silicon-organic liquid HSL-94 (HSL) based on ethyl hydride siloxane at room temperature according to the procedure described in [2, 4–6]. The composition of the triamon (T) in vapor phase corresponds to a chemical formula \[\[(\text{HOC}_2\text{H}_4\text{H})_3\text{N}^+\text{CH}_3\text{][CH}_3\text{SO}_3^-\] \] with low molecular weight radicals at the nitrogen atom. In opposite, the cation of the alcamon (A) contains a significantly greater hydrocarbon radical \(\text{C}_{17}\) [5]. Depending on the sequences and modes of chemisorption of QAC and HSL on the surface of the initial copper powder (Cu), the following samples were obtained: Cu/(A+T), Cu/A, Cu/HSL, Cu/T/A, Cu/A/T, Cu/T/HSL, Cu/A/HSL and Cu/T. The sample of Cu/(A+T) was obtained in a vapor mixture of A and T (1:1), Cu/T/A - by sequential layering of T/A.

Structural analysis performed by the laser diffraction method showed that modification of the powder (PMS-1) in A, T, HSL vapor does not lead to a noticeable change in the particle size and the specific surface; the specific surface was 0.16 ± 0.02 (m²/g). The bulk density of initial copper powder was 1900 ± 200 kg/m³. After the surface modification by the reagents the density remained at the range from 1900 to 2200 kg/m³. The density was measured by pycnometric method.

Determination of the amount of water vapor adsorption \(a_{\text{H}_2\text{O}}\) and measurement of adsorption isotherms for the studied samples were performed by a gravimetric desiccator method, varying the water vapor pressure \(P_{\text{H}_2\text{O}}/P_s = 0.45-1.00\), where \(P_s\) is the saturation pressure) at temperature of 20±2°C. Samples were weighed on a Shimadzu AUX220 analytical balance (accuracy 10⁻⁴ g). The relative pressure of \(P_{\text{H}_2\text{O}}/P_s\) in a desiccator was regulated by adding calculated amount of sulfuric acid into distilled water according to the procedure described in GOST 29244-91, and in [7]. The adsorption of water vapor by the samples was additionally controlled by the appearance and enhancement of intensity of the O1s peak (binding energy 532.5 eV) on XPS spectra, which is specific for water adsorbed on the metal [6, 8].

![Figure 1. Structure of Cu-powder on data of electronic microscopy.](image-url)
3. Results and discussion

The preliminary research has showed that adsorption isotherms of all samples refer to type III, according to paper [9], and have a sharp increase of the value of adsorption of water vapor (g/g) at relative pressure greater than 0.8. The steepest rise is observed for copper powder treated with organohydride siloxane in HSL vapor (the sample Cu/HSL). Samples Cu/A and Cu/T are sufficiently hydrophobic, since measurable adsorption is characteristic for relative pressure of at least 0.7. The most hydrophobic samples are Cu/A/HSL, Cu/T/A, Cu/(A+T) because the water sorption for them occurs only at ratio $P_{H_2O}/P_S$ greater than 0.82.

Interesting that the industrial hydrophobicizer HSL-94 [10], layered on copper surface without T or A sublayer, does not provide the maximum water-repellent effect (figure 2) and the sample Cu/HSL inferior in hydrophobicity to the samples with ammonium compounds on the surface, especially when interacts with saturated water vapor over 150 hours (figure 2).

![Figure 2](image)

**Figure 2.** Alteration of water sorption by copper-based samples from time of interaction with water vapor.

The time dependences of the sorption during long-term interaction (24 - 216 h) shows the complex oscillation damping process, which probably reflects sorption-desorption during surface saturation [2]. The description of these dependences by the superposition of a linear and Gaussian function provides an average relative approximation error of 6.2–9.7% (table 1). Generally, the accuracy of the approximation increases when a similar way is used for the parameter - 1/a. When describing the time dependence of the parameter 1/a, the approximation error decreases to 5.6 - 7.3% (tables 1, 2). This error is comparable by an order of magnitude with the measurement error of the sorption characteristics (3–5%) and does not exceed the confidence interval for determining the values of 1/a and a (figure 2). The calculation of the coefficients in the equations (table 1), were carried out in the software package MathCad. These coefficients are characteristic for modified copper-based samples. Exponents are used to describe the kinetics of sorption processes [11]. A variety of exponential equation were taken as a basis in the proposed description (table 1), which allows to take into account the extremum of a complex dependence. For the initial copper sample, this time is 96.4 hours (table 1), which is included in the exponent of the exponent part of the equation and practically corresponds with the time at which the maximum of the dependence $a=f(t)$ is observed experimentally (figure 2). The same for samples with layered ammonium compounds: Cu/(A+T) (curve 4) and Cu/T/A (curve 3). For these samples, the maximum ($t_m$) is 71.9 and 95.4 h, respectively, and is included in the exponent part of the equation.

It should be noted that in case of approximation of the experimental data on the sorption of water vapor on dispersed aluminum (PAP-2) with applied QAC using the Gauss function [6], the relative error for the dependence $1/a = f(t)$ 8.7%, and for $a = f(t)$ more than 10%.
As follows from table 1 the mathematical description of sorption properties of the samples Cu/(A+T) and Cu/T/A by linear function and Gaussian is quite satisfactory. However, inclusion of \( \ln t \) and \( t^2 \) into the equation is required for correct description of the properties of samples Cu/HSL and Cu/A/HSL. It is important to point out that the most hydrophobic samples (with lowest values of \( a_{\text{H}_{2}\text{O}} \)) have the highest level of nonlinearity of dependences \( 1/a=F(t) \) with minimum linear correlation coefficients (0.27-0.47) \[12\]. The increase of water-repellent properties of the samples is presented on figure 3. As follows, the sample (Cu/A/HSL) with silicon-organic outer layer and A sublayer is the most hydrophobic. It is important to underline the positive influence of sublayer (A or T), which was previously discovered \[2, 4\].

\[ \text{Cu/A/HSL} > \text{Cu/T/A} > \text{Cu/(A+T)} > \text{Cu} \geq \text{Cu/HSL} \]

Enhancement of hydrophobicity

Figure 3. The row of enhancement of hydrophobicity for \( t=145 \) hours.

Table 1. Mathematical description of time alteration of water sorption by copper-based samples.

| Sample          | Equations based on Gauss function | Average relative error, % |
|-----------------|-----------------------------------|---------------------------|
| Cu (PMS-1)      | \( a=0.165+1.26\cdot10^{-3} \cdot t+0.589\cdot \exp\left(-(0.025\cdot(t-96.4))^2\right) \) | 6.22                      |
|                 | \( 1/a=550-1.40\cdot t-320\cdot \exp\left(-0.256\cdot(t-95.1)^2\right)/1000 \) | 5.62                      |
| Cu/(A+T)        | \( a=-0.418+4.03\cdot10^{-3} \cdot t+0.383\cdot \exp\left(-0.011\cdot(t-71.9)^2\right) \) | 9.69                      |
|                 | \( 1/a=718-2.207-385\cdot \exp\left(-\frac{(t-71.6)^2}{10000}\right) \) | 7.09                      |
| Cu/T/A          | \( a=0.431-4.04\cdot10^{-4} \cdot t+0.383\cdot \exp\left(-(0.031\cdot(t-95.4))^2\right) \) | 7.33                      |
|                 | \( 1/a=232+0.259\cdot t-131\cdot \exp\left(-1.02\cdot(t-93.2)^2\right)/1000 \) | 7.29                      |
| Cu/HSL          | \( a=-0.143-1.033\cdot10^{-3} \cdot t+0.186\cdot \ln t-0.398\cdot \exp\left(-0.003(t-48.1)^2\right) \) | 3.09                      |
|                 | \( 1/a=454+0.56\cdot t-76.8\cdot \ln t+523\cdot \exp\left(-0.004(t-48)^2\right) \) | 4.64                      |
|                 | \( a=4.57+0.032\cdot t-6.12\cdot10^{-3}t^2-1.54\cdot \ln t+0.85\cdot \exp\left(-0.001(t-83.3)^2\right) \) | 5.78                      |
| Cu/A/HSL        | \( 1/a=-4.38\cdot10^{-3}-36.2\cdot t+0.07t^2+1.73\cdot10^3\cdot \ln t-674\cdot \exp\left(-0.0008(t-81.1)^2\right) \) | 9.78                      |

*Variable nondimensional magnitude \( t \) in the right parts of equations is specific time received by division \( t \) in hours for 1 hour.

Table 2. Correlation of water sorption (a) and parameter 1/a (calculated and experimental) for Cu/A/HSL.

| t, hours | 24   | 48   | 72   | 96   | 168  | 192  | 216  |
|----------|------|------|------|------|------|------|------|
| a, % (experiment) | 0.426 | 0.214 | 0.716 | 0.710 | 0.286 | 0.310 | 0.300 |
| a, % (calculated)  | 0.422 | 0.230 | 0.695 | 0.743 | 0.284 | 0.312 | 0.295 |
| 1/a, % (experiment) | 235  | 467  | 140  | 141  | 350  | 323  | 333  |
| 1/a, % (calculated) | 239  | 457  | 139  | 114  | 359  | 323  | 339  |
For the first time, the data obtained in this work on the sorption activity of surface-modified samples based on copper (PMS-1) can be compared with the known results of studying samples that also contain applied QAC, based on disperse aluminum (PAP-2) and copper powder PM-1 [2, 4, 5, 6, 12, 13, 15]. The comparison is interesting, due to the fact that the original PM-1 copper does not contain a stabilizing organic film on the surface (as in the case of PMS-1); Al-powder PAP-2 is stabilized in the industrial conditions with stearin, the film thickness of which, according to [6, 14], does not exceed 1-2 monolayers. Brief conclusions of the analysis are as follows. In samples based on PMS-1 and PM-1, the sample Cu/T/A is more hydrophobic (when comparing samples Cu/(A+T) and Cu/T/A). On the opposite for Al powder (PAP-2): the sample Al/(A+T) obtained in the vapor mixture of A and T is more hydrophobic and properties-stable [6, 10]. In case of application of ammonium sublayers under the outer layer of organohydride siloxane, on aluminum the sample Al/T/HSL becomes more hydrophobic, but not the sample Cu/A/HSL based on copper powder (figure 2).

In our opinion the observed differences is related to the structural correspondence of the surface of the initial metal substrate and the applied substances (QAC or organohydride siloxane) [2, 12]. In case of compliance, the applied layer of substance with hydrophobic hydrocarbon radicals strongly fixes on the surface; the application of two-component layers (T/A or A/HSL) seals the structure of the protective water-repellent layer on the metal, enhancing the hydrophobic properties of the sample. The chemical interaction of QAC with disperse metal is reliably recorded by X-ray photoelectron spectroscopy [12, 13]. The surfactants, which are used in production of PMS-1, according to GOST 4960-2009, are structurally similar to alcamon, which makes the sample Cu/A/HSL the most stable to water vapor exposure.

4. Conclusion

It was established that during long-term (24-216 h) interaction of saturated water vapor with surface-modified powders based on copper PMS-1 under static conditions, the amount of water sorption (a, g/g) changes in a complex way, similar to damping oscillations. A mathematical description of the process, which allows to approximate the experimental data on the time dependences a=f (t) and 1/a=F(t) based on the linear and the Gauss function with the relative error of 5–7% is proposed. The description has a relative simple physical meaning and allows to make quantitative assessments of nonlinear effects in the systems. The row of enhancement of hydrophobicity depending on the mode of metal surface modification was established.

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