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Evolution of the Metallic Copper Surface at the Oxidation in CCl_4–DMF

S. V. Panteleev[a], S. V. Maslennikov[a], I. V. Spirina[a], S. K. Ignatov[a], and M. A. Isakov[b]

[a] *Research Institute for Chemistry at Lobachevskii Nizhny Novgorod State University,*
Gagarin av. 23/52, Nizhny Novgorod, 603950 Russia

[b] *Physico-Technical Research Institute at Nizhny Novgorod State University, Nizhny Novgorod, Russia*
e-mail: pasv7@mail.ru

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Abstract—The evolution of the compact copper surface at the etching in the system of CCl_4–DMF with a concentration of carbon tetrachloride ≈ 1 M was studied using atomic force microscopy (AFM). The dependence of the copper etch in a rate on the time and the concentration of the oxidizing agent (carbon tetrachloride) was measured. The dynamics of formation and destruction of active centers in the reaction was investigated.

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It is known that in the system of metal–oxidizer–solvent the surface reactions occurring at the interface between the reacting solid–liquid phases play a major role [1–7]. The reaction series, including a compact metal, organic or organoelemental halide, and a dipolar aprotic solvent, belong to the so-called Grignard-like systems [8]. To date, extensive experimental and theoretical data on the kinetics of oxidative dissolution of metals in these systems were accumulated, and the composition and structure of the products and intermediates of the reaction were analyzed, simple schemes of the reaction path, including, as a rule, the adsorption of reagents on a solid surface, were proposed. However, such consideration of the Grignard reaction and related processes is rather simplified, because it does not consider that the main (rate-determining) act at the surface and the formation of the transition state occur in the local vicinity of active reaction sites or directly on them. The present study is aimed to track the changes in the surface morphology of compact copper in the process of dissolution (oxidative etching) in the CCl_4–DMF system by determining the surface roughness and height differences on the border between the metallic specimen and the inert substrate, using the atomic force microscopy (AFM) technique. The interaction of a metals M with carbon tetrachloride in aprotic solvents L was investigated experimentally [9–11]. In general, this reaction can be written as:

$$\mathrm{M} + \mathrm{CCl_4} + \mathrm{L} = [\mathrm{CCl_3MCl} \cdot \mathrm{L}]\ (\text{solvate}). \qquad (1)$$

Typically, the reaction is accompanied by the formation of a large number of related by-products, including $CCl_2M_nCl_2$, C_2Cl_6, C_nCl_m (oligomer), and MCl_x. All of these compounds were found by chemical analysis: elemental analysis, gas chromatography, and mass spectrometric methods. The system of M–CCl_4–L is Grignard-like one: in the absence of coordinating donor solvent reaction (1) is very slow, even at elevated temperatures. As is found, in the case of magnesium the oxidation proceeds at room temperature with the highest rate in DMF and in the case of copper, in DMSO [11].

We studied the morphological changes of the copper surface in DMF medium. We used this solvent for several reasons. Firstly, the oxidative dissolution in this solvent occurs with a significant rate even at room temperature. Secondly, this solvent was used in most previous studies, so a comparison was possible.

The reaction of the type (1) and similar processes are complicated by marked induction period at the initial stage [12, 13], which can be reduced by special mechanical or chemical treatment of the surface of the oxidized substrate, or by the introduction additives of the reaction products to the original reaction mixture [12]. This fact is usually explained by the removal of the surface oxide–hydroxide film [14, 15]. It points to the important role of the state of the interphase region at the contact of reagents. After the start of the reaction it proceeds relatively fast with a compact non-oxidized metal.

The problem concerning effect of the coordinating solvent on the reaction is rather complex and is not fully solved [8, 13]. The coordinating solvent influences the course of the reaction, in part, through the transfer of electron density from the adsorbed molecule to the metal. The latter then becomes negatively charged relative to the adsorbate [8], which leads to a decrease in the electron work function from the metal surface and thus makes easier its interaction with the oxidant molecule. These assumptions have been fully confirmed in [8], where the effect of adsorption of acetonitrile, ether, THF, DMF, and pyridine on the electronic structure of the compact metal, simulated as a molecular cluster was analyzed.

The adsorption of electron-donor molecules was found to be accompanied by a strong electron-electron relaxation of the cluster electron levels and the appearance of the areas with abnormally high electrostatic potential and charge density, and these areas correspond to the neighborhood of the adsorbed molecules. It was indicated in [16] that the adsorption of a coordinating solvent causes additional energy heterogeneity of the surface due to the influence of adsorbed particles on the electronic levels of its active sites.

The rate of the metal oxidation depends on many factors, including among them the state of the metal surface. It is known [4] that the magnesium surface is mostly unreactive, and the Grignard reagent is formed in relatively small areas of the metal surface. The results of [17] confirm these observations. When a 2.5 M solution of ethyl bromide in THF is used as an oxidizing agent, in the developed process the surface density of the reaction sites was ≈ 150 cm^{-2}. In this case, the concept of active sites, which was ignored in almost all studies [4, 6, 18–22] because of the complexity of the problem, is crucial for considering the nature of the surface reactions.

In [23] on the basis of quantum-chemical calculations of magnesium clusters with distorted structure of the external atomic layer and the calculation of the thermodynamic energy of the atom separation from the surface a simple interpretation of an active site was formulated. The active site is a high-energy structurally loose (with a sufficiently large number of atoms with low coordination number) defect of the *pyramid* or *tower* type, which is a crystalline scaffold with a continuum-distorted geometry as compared with an *ideal* structure.

Thus, the active site is a physical or chemical defect of the metal surface, where the main rate-determining act occurs and the activated complex is formed. Active sites react first, leading to the formation of new sites with high reactivity. The active sites and the defects with low reactivity are able to regenerate, so that their ratio is maintained approximately constant [7].

Solving the problem of active centers would facilitate understanding the mechanism of the formation of the Grignard reagent by the direct oxidation of the metal in coordinating medium, and most importantly, to reveal the nature of the surface reaction. Furthermore, the concept of active sites is also a key in heterogeneous catalysis, which is important from the point of view of the theory and practice of heterogeneous catalytic processes.

In this work, atomic force microscopy was used to study the surface of metallic copper. It was The roughness and the distribution curve on height of the number of surface defects in a compact state and after etching in a mixture of CCl_4/DMFA at various time intervals were estimated, the kinetics of the oxidation process were studied by measuring the height difference at the metal–substrate interface in the systems with constant composition and different time of exposure of the metal to the oxidant, as well as for systems with variable composition and fixed (≈ 5 min) reaction time.

At the development of the oxidation process side effects appear that affect negatively the reliability of the results obtained: the surface gets covered with a layer of poorly soluble oxidation products (including oligomers and salts) that prevent further reaction. In addition, due to the nonuniform oxidation, in some areas abnormally deep craters and fissures appear, increasing sharply the total contact surface of the reagents leading to dramatic acceleration of the reaction. The superposition of these two effects (surface deactivation because of the deposition of poorly reacting products, and the *cratering* due to the presence of highly reactive sites) contribute to the impossibility of quantitative conclusions on the state of the surface and the reaction rate at the large-time oxidation (conventionally, more than 5 min).

The original copper surface had the expected polycrystalline structure, as shows Fig. 1, with typical lateral grain size ~120 nm. The grain boundaries are clearly visible in the contrast of the lateral force (Fig. 1b).

Holding samples in a solution of CCl_4 in DMF with a concentration of carbon tetrachloride 1 M for 1.5 min (298 K) results in a sharper distribution curve, shifted to lower heights (Fig. 2). For example, the number of defects with a height of 60 nm in the area of 10×10 μm decreased almost 2.5 times. The height distribution Gaussian shifted after etching to the left by about 5 nm relative to the height distribution function of the initial surface of the copper sample. The value of the standard deviation (RMS, root mean square), the main indicator of surface roughness, was 10.29 nm before etching and 8.86 nm after the reaction.

In the reaction course the defects with the maximum height, which are supposed to be the least stable, reacted the first, resulting in a decrease of the surface roughness. Thus, the most reactive in the initial stage of the reaction are large (conventionally, over 40 nm) and extra large (conventionally, over 60 nm) defects (active sites) of the *pyramid* type. Just these defects of the compact copper surface are a major source of reactivity. Thus, the *n*-atomic defects ($n \approx$ 100–150) that presumably include copper atoms with low coordination numbers react initially, They are the primary target atoms in the surface reaction.

To study the changes in the copper surface in the reaction with CCl_4 in DMF at the atomic level five scans were performed during the reaction process with different time intervals: 0, 20, 50 s, 2, and 5 min, with a resolution of 250×250 nm. The average surface profiles corresponding to the compact non-oxidized sample and the samples after different times of exposure the sample to the reaction mixture are shown in Fig. 3, together with the histograms for the three scans.

While considering histograms and averaged profiles in Fig. 3 it can be seen that the state of the copper surface during the oxidation process undergoes significant changes. Key indicators of surface roughness change nonmonotonically. In particular, after 20 s exposure of the system to the reaction mixture the fraction of defects on the heights markedly narrowed and shifted to higher heights. After keeping the sample for an additional 30 s, the fraction enriched with surface disorders with even greater heights. In this case, at the atomic level the surface becomes of granular structure due to selective etching, and is coated with a network of *n*-atomic defects. As a result, on the surface profile *ripples* are observed with a height difference of 0.3–1 nm, which probably correspond to the most effective reaction zone.

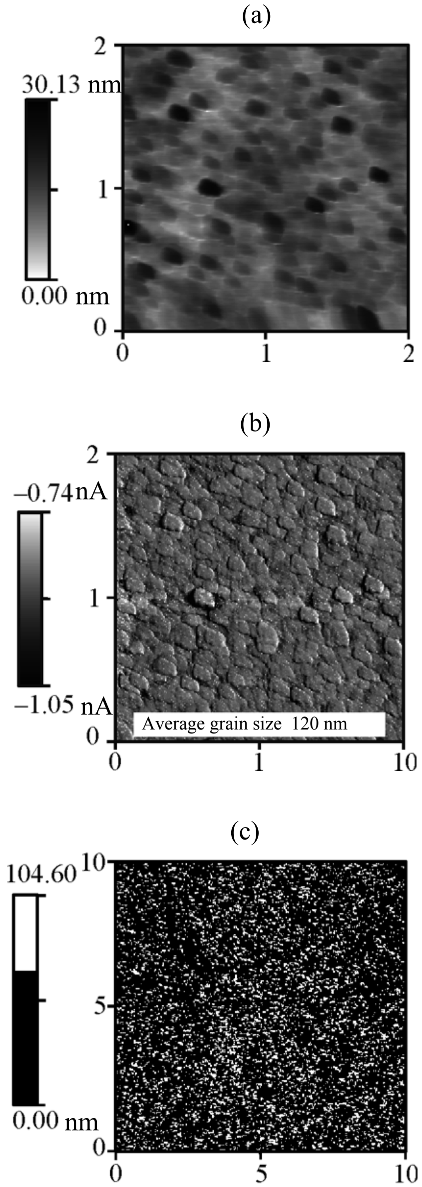

Fig. 1. Topography of the surface of copper sample used in the study of the “life cycle” of active sites, (a): 2×2 μm; (c) 10×10 μm, and the map of lateral force, (b) 2×10 μm.

Such a small etching time (less than 1 min) probably corresponds to the induction period, associated with the removal of the surface oxide film. However, it is known that the oxide film on the copper surface is not even, and has discontinuous areas, so the sample subjected to etching can be very nonuniform in the initial stage, as is observed in reality after a sudden change in the surface profile. After 50 s of etching, on

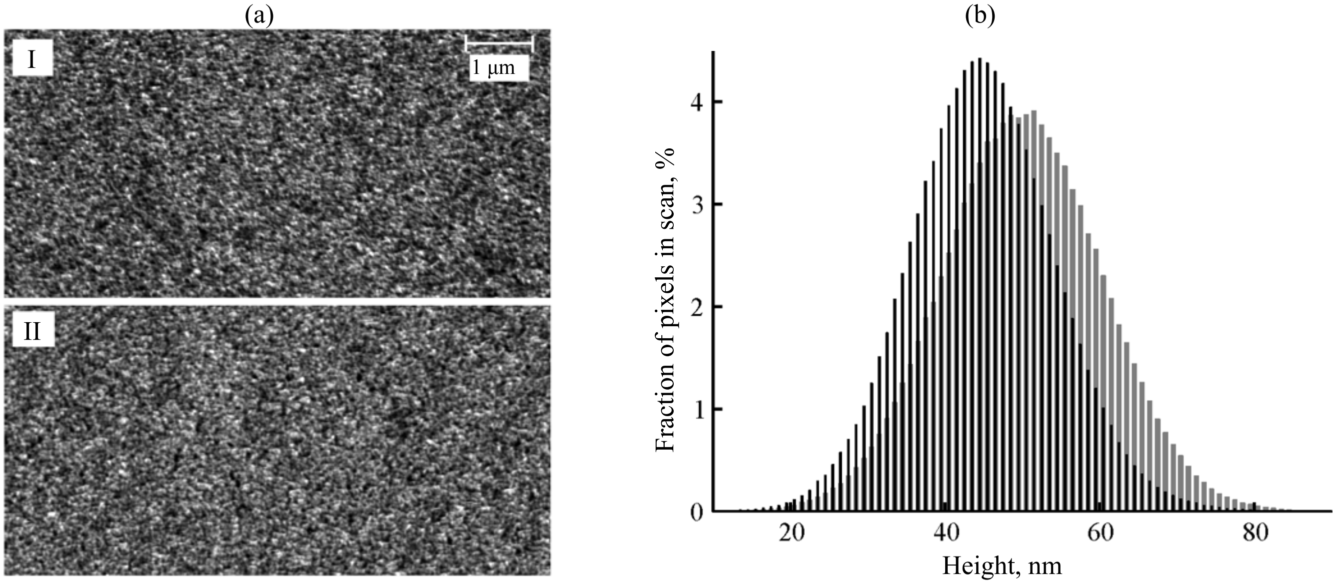

Fig. 2. Topography of the surface of copper sample (10×10 μm) before etching [(a), I] and after 1.5 min exposure in the mixture CCl_4–DMF at the oxidant concentration 1 M [(a), II], and Gaussians of heights distribution of the corresponding states (b). After etching the curve displaced to the side of amaller heights by about 5 nm.

the sample surface the defects dominate exclusively of micron and submicron size. The curves in Fig. 3 for etching during 2 and 5 min indicate that the reaction reached a steady state: the surface becomes more homogeneous, as indicated by the decrease in RMS in the fifth minute of the reaction, and the histogram of the surface profile becomes close to the histogram of the non-oxidized compact copper. The peak blur should be attributed to the erosion of the metal sample, precipitation on the surface of heterogeneous and sparingly soluble dense adsorbed film of the reaction products. For deeper conversion ($t \geq 10$ min) it is incorrect to draw conclusions about the state of the copper surface in the contact area with a mixture from the curves of distribution and average profile, as they begin to include a variety of components. Moreover, monitoring the state of the surface of samples with high optical zoom (×120) showed that the surface etching was very nonuniform: in some areas, probably cracked, the sample was fully oxidized, up to the substrate. In the area of the copper contact with glass a cavity may appear to which the solvent molecules and oxidant can penetrate causing additional internal etching. These factors cannot be taken into account, and they are the source of the error. The above said is confirmed by the fact that at a prolonged exposure of the sample to the mixture the metal is separated from the substrate. The dependence of the surface roughness on the copper etching time (Fig. 4) includes three distinct areas, the last of which corresponds to reaching the steady state after the highest point.

The results of AFM studies of the evolution of copper surface at its oxidation in CCl_4 are highly dependent on the size of the scan area. For the scan area 10×10 μm the outer atmosphere and the transition from the induction period to the steady state reaction is very smooth. At the (pseudo)atomic resolution (250×250 nm) these effects lead to an abrupt change of surface roughness as a function of the reaction time.

It must be assumed that the reactivity depends on the steric structure of the defect rather than on its size. The atomic framework configuration promotes the approach to the reaction site of the oxidant molecules at a distance sufficient for the formation of the transition complex and fulfillment of the chemical act. In this case the activation barrier to the atom (cation) abstraction from the reaction site and embedding it in the transition complex should be minimal. Only these two conditions ensure a high reactivity of the defect surface, in addition to other factors providing the very formation of the defect. It should be noted that such a short reaction time (within 5 min) must include the induction period, therefore the true reaction time is smaller.

Study of the kinetics of copper oxidation by the atomic force spectroscopy. To study the rate of the copper oxidation we used an original technique of

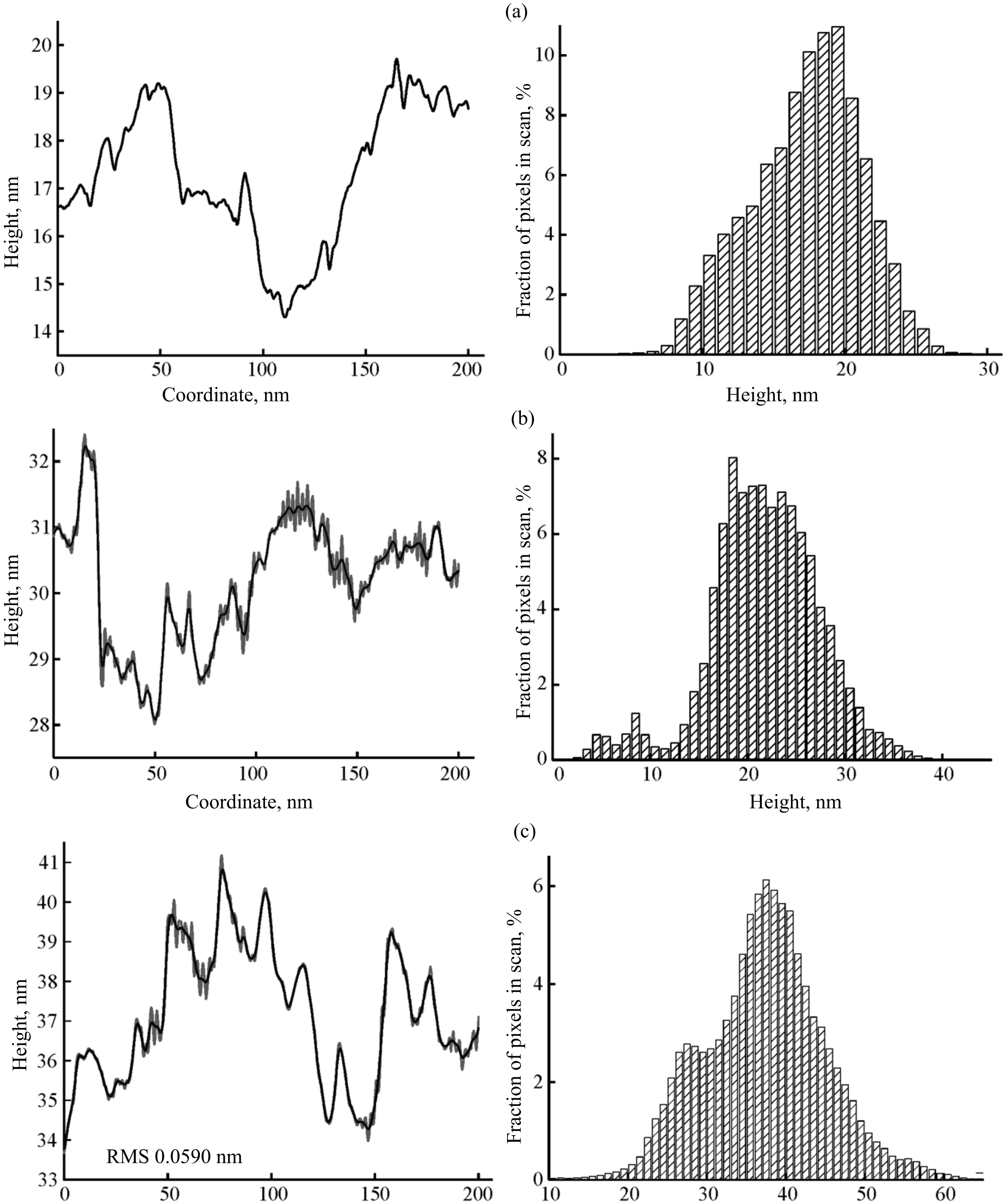

Fig. 3. Average profiles (at left) and distribution curves of the defects number on heights on the surface of the copper sample (at right) for the scan area 250×250 nm: (a) initial sample; (b) after 20 s of the contact with the reaction mxture CCl_4–DMF; (c) after 50 s of the contact (T 298 K, c_{Ox} 2 M).

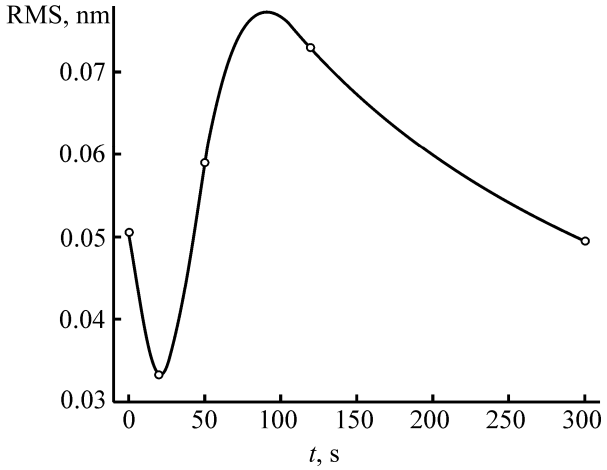

Fig. 4. The dependence of the roughness of copper surface approximated by the root-mean-square value (RMS) on the reaction time (T 298 K, c_{Ox} 2 M).

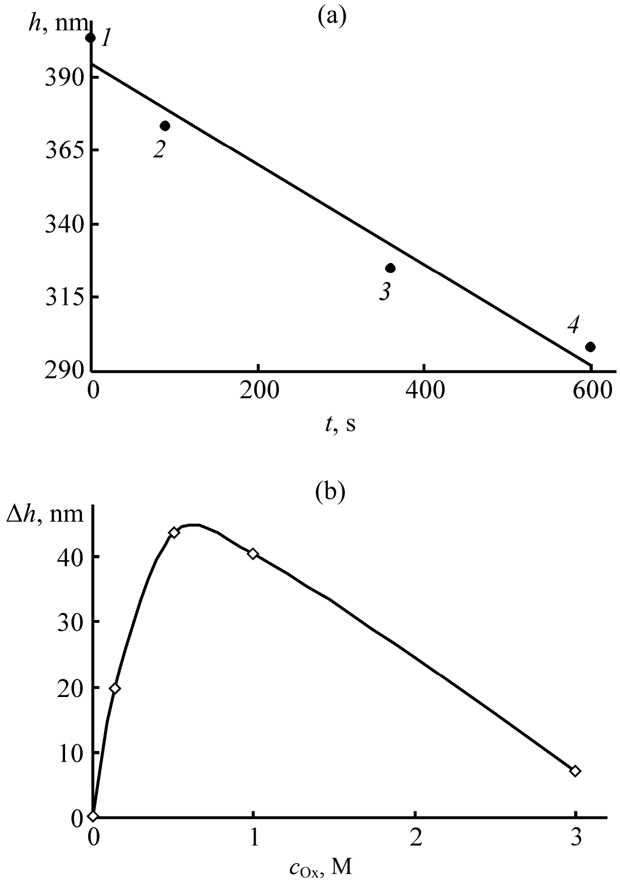

Fig. 5. The depdndence of the height (h) of the copper sample on time t of the oxidative action of he mixture CCl_4–DMF (c_{Ox} 1 M, 298 K). (*1*) compact nonoxidized sample; (*2*) after 1.5 min; (*3*) after 6 min; (*4*) after 10 min (a) and the heights variation at the boundary copper–glass at the oxidation with the mixture CCl_4–DMF as a function of the carbon tetrachloride concentration ($c_{\mathrm{DMF}} >> c_{\mathrm{CCl4}}$; c_{DMF} = const, T 298 K) (b).

kinetic analysis that previously was not mentioned in the literature. The control over the rate of reaction of the solid phase was carried out using atomic force microscopy at the permanent metal–substrate contact at the interface. The kinetic experiment involved the measuring changes in the sample film thickness during the oxidation. The changes in the sample thickness makes it possible to determine the nature of the oxidative dissolution of copper. Obviously, this method can be applied to study the dynamics and kinetics of other heterogeneous reactions, e.g., estimation of the rate of oxidative dissolution of the solid films, in particular, of nickel, iron, palladium, platinum, silver, gold, and their alloys. The important condition is the possibility to control the linear dimensions (height, diameter) of the samples. To minimize the error associated with the incompleteness of the reaction and separation of the insoluble film of non-reactive products on the test surface, the nominal step of the metal–substrate height should be in the range of 0.1–1 μ, and the width of the area of transition the metal in the substrate 20 μm or less. For the more active metals (magnesium, aluminum, zinc, etc.), this method is of little use, because of the formation on the surface of the oxide–hydroxide layer. The rate of its destruction can be comparable to that of the main process (metal dissolution).

The dependence of the height (h) of copper films (step height) on the reaction time is shown in Fig. 5a. This is a straight line with a fairly high correlation coefficient (0.969) that obeys the following regression equation:

$$h = –0.17\ t + 394.51.$$

Using similar technique to measure height differences on the metal–substrate boundary at the etching the copper sample with a nominal height of 410 nm for 5 min by CCl_4 solution in DMF with different concentrations of oxidant at 298 K we obtained the dependence of the process rate on the oxidant concentration in the reaction mixture. The form of dependence is shown in Fig. 5b.

This dependence suggests that the interaction of copper surface with the oxidant may be of the order with respect to the oxidizer close to the first and pseudo-zero order with respect to the oxidized metal at low concentrations of oxidant, when the reaction is not complicated by secondary processes. This corresponded to the data of [11], where it was also revealed by resistometry that the reaction with metallic copper was first order with respect to CCl_4.

Thus, the maximum rate of oxidation of copper is observed in the solution with the CCl_4 concentration 0.5–1 M. As the concentration of the oxidant grows, rate of change in the profile height at the metal–substrate boundary slows dramatically. This fact may be due to the deposition of low reactive transformation products on the copper surface, hindering the access of reagents to the reaction sites and reducing the rate of oxidative dissolution of copper sample.

As the reaction on the metal–glass boundary develops, the boundary, whose nominal width is about 16 μm, becomes less sharp: in 1.5 min of reaction it is 18 μm, in 6 min, 25 μm, in 10 min, more than 40 μm. The broadening of the metal–substrate boundary indicates a high reactivity of the boundary zone and intense oxidative etching, leading to smoothing the sample edges. At the tenth minute the boundary is so broad that it is difficult to identify the region of the transition of the metal in the glass. In addition, the boundary becomes very rugged. This is further evidence of the high nonuniformity of the oxidation process.

EXPERIMENTAL

Samples of copper used to study the kinetics of surface oxidation were round films of the diameter ~0.25–1.00 mm formed on a thin glass substrate with a molybdenum mask pressed to it, by thermal evaporation in a vacuum. The residual gas pressure in the growth chamber was $p_g \approx 4\times10^{-6}$ Torr, the growth rate was estimated at the level $V_g \approx 1–1.5$ nm s^{-1}. The Initial thickness of the copper film was $d \approx (410 \pm 10)$ nm.

The oxidation of copper was carried out in air using the systems CCl_4–DMF with different concentrations of carbon tetrachloride: 0.1, 0.5, 1, 2, and 3 M. Sample was immersed in the solution, which was stirred vigorously to weaken the diffusion component of the reaction and approaching the process to the kinetic regime. As CCl_4 is weakly associated fluid, as evidenced by high volatility and low boiling point, and carbon tetrachloride molecules are very poorly solvated, as evidenced by the small enthalpy of mixing [24], the CCl_4 molecules freely move at a rate close to that of the mean free path in the pure solvent. Consequently, the rate of diffusion of the oxidant molecules to the copper surface is high and unlikely to limit the rate of the reaction at low concentrations of DMF (conventionaly, 1 M).

The oxidation time was controlled by a digital timer. After the reaction, the sample was thoroughly washed with diethyl ether and hexane. After complete evaporation of the solvent from the surface in the area active air flow, the sample was studied by atomic force microscopy (AFM).

AFM studies were carried out using a scanning probe microscope (SPM) Solver Pro, manufactured by NT-MDT (Zelenograd, Russia) in atmospheric conditions using I-shaped silicon cantilevers NT-MDT NSG-11 with a tip curvature radius $R < 10$ nm (according to the instrument passport). To study the topography of the surface a 2×2 μm^2 scanner was used in the mode of scan by sample. The instrument was calibrated periodically in the x, y and z coordinates with test structures NT-MDT TGZ-3 and TGT-1. Processing of the results of the AFM studies was performed with the special software for data processing and analysis NT-MDT NOVA Image Analysis 2.0 and Veeco Instruments (USA) SPMLab 6.02.

To scan the surface visually uniform sites were selected not containing the macroscopic defects of any kind, like chips, cracks, and impurities. To standardize the selection of the surface area on the sample labels (heterogeneities) were selected under optical zoom 120×, relative to which the probe was located. The accuracy of the position of the labels on the display was of the order of 1 mm, that corresponded to 8 μm in real scale. Also the sample film thickness was measured after etching by scanning the region of the copper–substrate border.

All scans were obtained with a pixel resolution of 1024×1024 at a frequency of scanning 0.5 Hz.

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