

Effect of Mechanical Treatment on the Reactivity of Copper Powder toward Acetic Acid

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Abstract—The mechanism of the mechanical activation of copper powder is studied by calorimetry, XPS, and X-ray diffraction. The increase in the heat of copper–acetic acid reaction caused by mechanical treatment is due to the activation of dioxygen involved in this reaction. This activation is due to the presence of suboxide oxygen with an increased electron binding energy in mechanically treated copper.

The conventional base components of oxidation catalysts are fourth-row transition-metal oxides and platinum-group metals. In general, catalytic activity may be due to either regular or defect surface sites, depending on the type of catalyst and reaction. Therefore, the reactivity and, accordingly, the catalytic properties of a catalyst can be controlled by varying the surface concentration of defects and surface microstructure. Typical examples of defect-rich materials are ultrafine metal [1] and ceramic [2] powders, which differ markedly in their properties from coarse powders and monoliths. This difference is primarily due to the excess surface energy, which upsets the balance of forces and masses, breaks the symmetry of their distribution, and changes equilibrium interatomic distances relative to their values in the corresponding macrocrystals (normal relaxation takes place). Other effects of the excess surface energy are shear strain, changes in the atomic motif of crystal faces, and the “smoothing-away” of vertices and edges through small angular deformations of interatomic bonds (tangential component) [1]. The difference in bond length causes a difference in reactivity: nanoparticles are more readily oxidizable than macrocrystals and sinter at extraordinarily low temperatures, with self-heating [3].

Ultrafine metal powders can be prepared by electric explosion of a wire (EEW) [3]. This method affords fine metal particles in which nonequilibrium states with strained bonds are conserved, since the particles cool very rapidly after the explosion. Strained bonds in solids can be obtained by mechanical treatment as well [4, 5]. Mechanical treatment of a very plastic material causes this material to flow and leads to structure disordering. This results in disturbed zones with a high dislocation concentration. Thus, part of the energy delivered by the mechanical activator is converted into the energy of dislocations and other structure defects. The energy accumulated by the material can be released in

various physical processes to alter the physical and chemical properties of this material.

Mechanical treatment of copper metal in the presence of dioxygen, including dioxygen adsorbed on the surface, can yield surface oxides with various concentrations of defects, which enhance the activity of copper-metal-based catalysts in oxidation reactions. Investigation into the action of copper-containing catalysts in redox reactions has demonstrated that the catalytic activity peaks together with the amount of metallic copper that has resulted from the interaction between the catalyst and the reaction medium [6, 7]. Furthermore, the heat of the copper–acetic acid reaction is greater for copper powder obtained by the EEW method than for a copper monolith [8]. It follows from these findings that copper metal as a catalyst for redox reactions deserves as much attention as the oxidized forms of copper.

A number of studies have been devoted to the effect of mechanically induced lattice microdistortions on the properties of copper metal [9–11]. However, no information has been reported as to the effect of mechanical treatment (elastic and plastic deformations) on the reactivity of copper.

In view of this, investigation of the effect of mechanical treatment on the reactivity of copper is of great scientific and practical significance.

In the design of our experiment, we proceeded from the following hypothesis: surface oxides that result from the mechanical treatment of a copper powder in the presence of O₂ (atmospheric and/or adsorbed) can affect the reactivity of this powder in oxidation reactions. Since the surface oxides do not form regular structures, they are amorphous to X-rays; as a consequence, electron microscopy and X-ray diffraction, which are the methods most widely used in the characterization of solids, are incapable of providing essential information concerning mechanically induced structural changes in copper powder (see below). In view of

this, it is necessary to find an appropriate method for the investigation of the effects of mechanical treatment. Here, we report the accumulation of mechanical energy by copper powders and the reactivity of mechanically treated copper powders in terms of the heat of reaction between these powders and acetic acid. The reaction between copper metal and acetic acid in the presence of dioxygen, yielding basic copper(II) acetate (verdigris, $\text{Cu}(\text{OH})(\text{CH}_3\text{COO})$), is well known from the literature [8, 12]. This reaction is very convenient for thermodynamic studies since it is not accompanied by any uncontrollable processes changing the enthalpy of the system, such as precipitation or gas evolution.

EXPERIMENTAL

We examined copper powder with a dendrite structure and a specific surface area of $0.16 \text{ m}^2/\text{g}$ (PMS-A brand, Soviet Standard *GOST 4960-75*). Mechanical treatment was carried out in an AGO-2 centrifugal planetary mill [13]. The power delivered by the balls was 55 W/g (40 g). Powders were milled in a steel or copper drum filled with air or argon, using, respectively, steel and copper balls 5 and 7 mm in diameter. The weight of the balls was 200 g, and the weight of the powder was 10 g. After the powder was milled for 30 s, the mill was stopped for 2 min to cool the milled material and balls. This procedure was repeated until the preset duration of milling was reached.

The reactivity of copper powders was evaluated as the heat of their reaction with glacial acetic acid at $T = 80^\circ\text{C}$. The heat of reaction was measured using an MKDP-2 Calvet-type microcalorimeter (Institute of Chemical Sciences, Siberian Division, Russian Academy of Sciences). The weight of a copper sample was 25 mg, and the volume of acetic acid was 2 ml (at $T = 20^\circ\text{C}$). Before the reaction, the cell with the reactants was thermostated for 2 h. The reaction was initiated by bringing the reactants into contact; after that, the reaction mixture was continuously stirred. The weight of reacted copper was determined gravimetrically, taking into account the unreacted copper in the cell. We examined both fresh copper samples and samples that were held in air at room temperature for various periods of time up to 3 months. At least three measurements were taken at each reaction time point. The spread of experimental data was no greater than 5%.

The specific surface area of powders was determined by the BET method from thermal argon desorption data, using an internal standard [14]. Before measurements, all samples were heated in flowing Ar or He at $T = 120^\circ\text{C}$ for 0.5 h. The error in BET measurements did not exceed 7%.

The optical density of copper solutions in acetic acid was measured with an FEK-60 photoelectric colorimeter and a nephelometer, using a light filter with maximum transmittance at 590 nm.

Structural changes induced in copper powder were studied by X-ray diffraction (DRON 4.0 diffractometer, monochromated CuK_α radiation; synchrotron radiation with a wavelength of 1.5406 \AA). Experimental data were fitted to a pseudo-Voigt type 1 function. Reflections were located as peak positions. The error in peak position was no larger than 0.01%.

XPS studies were carried out on a VG ESCALAB HP electron spectrometer operated in the constant analyzer energy mode, using AlK_α polychromatic radiation ($h\nu = 1486.6 \text{ eV}$; 200 W). The binding energy (E_b) scale was preliminarily calibrated against the ground states of gold and copper ($\text{Au}4f_{7/2}$, 84.0 eV; $\text{Cu}2p_{3/2}$, 932.67 eV). Samples were secured on a holder using a double-faced conducting scotch. The charging effect during photoelectron emission was taken into account by using the $\text{C}1s$ line of hydrocarbon inclusions (284.8 eV) as an internal standard.

XPS spectra were recorded either throughout the spectral range (at an analyzer energy of 50 eV) or in selected regions (at an analyzer energy of 20 eV). Relative element concentrations in the material were determined up to a depth of 20–40 Å from the integrated intensities of photoelectron emission lines corrected for atomic sensitivities [15]. For detailed chemical analysis, we deconvolved the spectra into components.

After subtracting the background by the Shirley method, the resulting curve was decomposed into a number of lines due to electron emission from the core levels of atoms in different chemical environments. Peak contours were approximated by mixtures of Lorentzian and Gaussian functions. The depth profile of concentration was studied by layer-by-layer analysis. The surface was sputtered by argon ions with an energy of 2.5 keV. The sputtering rate was 1–2 nm/min [15].

RESULTS AND DISCUSSION

It seems pertinent to make some comments concerning our experimental procedure before presenting calorimetric data. Once the mechanical force exerted by the activator is removed, stress relaxation begins. This includes the recombination of free radicals and ionic species, dislocation annihilation or outcrop, etc. The rates of these processes may vary significantly, depending on aging conditions and the nature of the material, and are difficult to estimate. Aging may take a long time. In view of this, copper powders were examined both immediately after milling and after they were aged in air at room temperature for some time up to 3 months. It was found that, under these aging conditions, the powders undergo no changes that can be detected by the above experimental methods. The samples that were prepared after the establishment of this fact were characterized by all of the above methods after aging periods of no longer than 3 months.

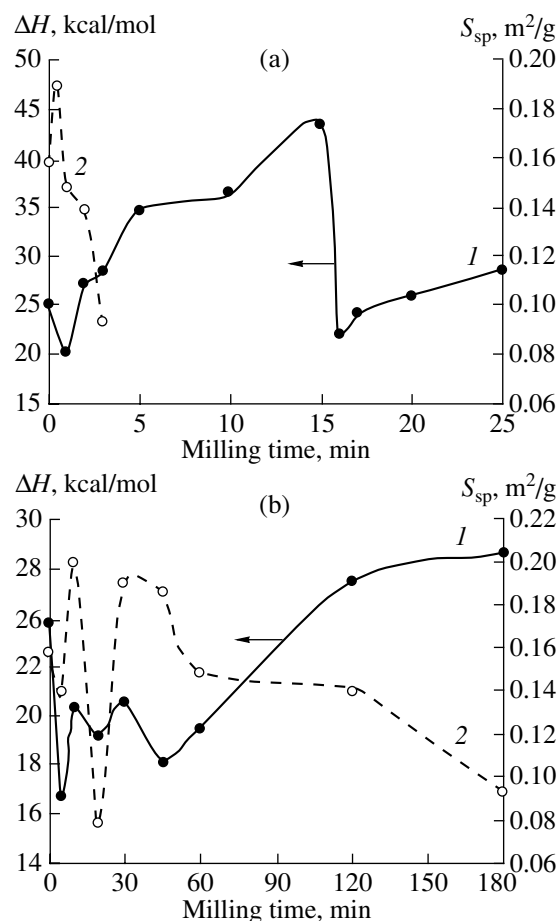


Fig. 1. (a) (1) Heat of reaction between milled copper powder and (2) the specific surface area of this powder as a function of milling time. (b) Initial portions of curves 1 and 2.

The relaxation of mechanically induced nonequilibrium structures can take place directly during mechanical treatment if energy is continuously delivered. Some parameters of the material, including the heat of solution [16], undergo cyclic changes during mechanical treatment, while others, including dissolution rate [17], pass through an extremum.

In the initial experiments, we used copper drums and copper balls varying in size from 5 to 7 mm. When milling was performed for 3–5 min or a longer time, the unwanted phenomenon of particle aggregation was observed: considerable amounts of the powder stayed on drum walls and balls as a lining. This effect altered the inner diameter of the drum and the diameter and weight of the balls, thus modifying the initial milling conditions. In subsequent experiments, milling was performed in a steel drum with steel balls 5 and 7 mm in diameter. The inner surface of the drum was preliminarily lined with copper by milling a copper powder in an inert (argon) or reductive (diethylamine) atmosphere for 10 min or a longer time. In subsequent milling runs, this lining did not cause any considerable sticking of

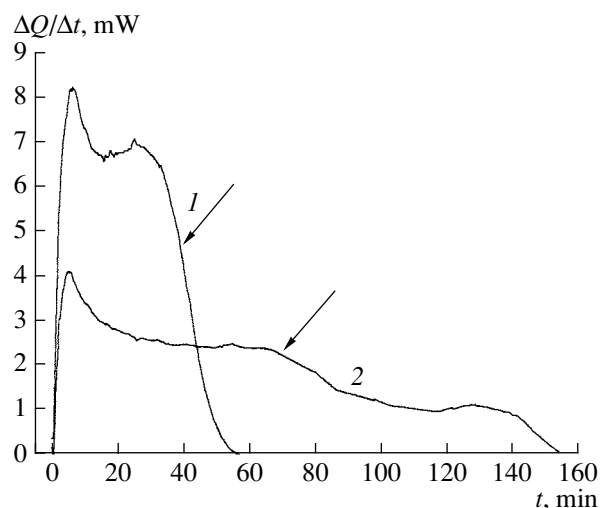


Fig. 2. Kinetics of heat evolution in the copper–acetic acid reaction: (1) initial copper powder and (2) the same powder milled for 3 min.

copper powder onto the walls and balls and did not thin away.

Analysis of calorimetric data obtained with copper and steel drums demonstrated that, within the calorimetric error, the heat of reaction between copper and acetic acid is independent of the structural material of the drum and balls.

Below, we report the main calorimetric data for the reaction between acetic acid and the original copper powder and for the same reaction involving copper powders milled for various periods of time.

(1) It was found that the copper powder being milled accumulates the mechanical energy delivered by the activator: milling for 15 min increases the heat of copper–acetic acid reaction from 25 to 45 kcal/mol (Fig. 1). This large amount of accumulated energy cannot be due to lattice disordering alone. The causes of this rise in the heat of reaction are discussed in greater detail below. Furthermore, it was established that the heat of reaction is higher for a coarser fraction of activated copper powder than for a finer one. Hence, it was inferred that most of the energy is accumulated by coarse particles.

(2) As follows from the kinetics of heat evolution in the reaction between acetic acid and milled copper powder, defects build up in the metal bulk during milling. This is indicated by the increase in both reaction time and the heat of reaction together with the fact that the specific surface area of the powder milled for >1 min is larger than that of the original powder (Fig. 2). By reaction time, we mean the time it takes for the heat of reaction to fall to instrumental zero in the calorimetric procedure described in the previous section. The specific surface area of the sample milled for >3 min was not measured, because, due to particle aggregation, its value was beyond the measurement

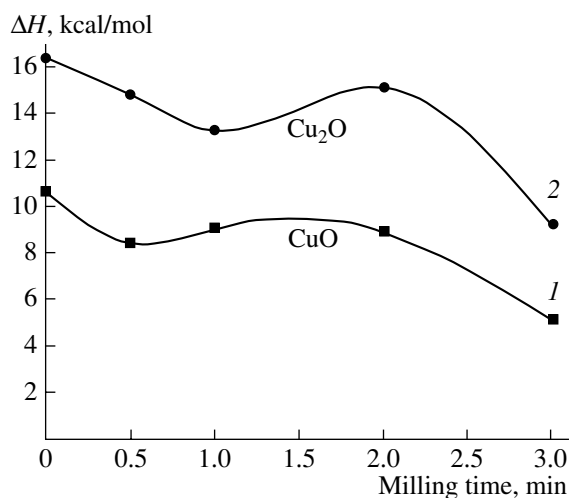


Fig. 3. Heat of reaction between acetic acid and milled (1) CuO and (2) Cu₂O as a function of milling time.

range of our experimental setup (at an allowable error of 7%). Thus, the specific surface area of the sample milled for >3 min is below 0.08 m²/g.

(3) Relaxation of bulk defects was observed in copper powders milled for >15 min (Fig. 1). The shape of the heat of reaction versus milling time curve suggests that the accumulation and relaxation of structure defects responsible for the heat of this reaction make up a cyclic process. However, we did not carry out any special investigation in order to verify this hypothesis. The cause of this phenomenon remains unclear.

(4) The increase in the heat of copper–acetic acid reaction that is due to milling cannot be explained in terms of CuO and Cu₂O resulting from the mechanically induced oxidation of copper, because the heats of reaction between these oxides (including mechanically treated specimens) and acetic acid do not exceed

17 kcal/mol and decrease as the activation time is lengthened (Fig. 3).

The results indicating that the copper powder being milled accumulates energy suggest that milling changes the reactivity of the copper powder toward acetic acid. Although the calorimetric technique used in our previous studies [18–21] allows kinetic measurements to be performed, the most precise data can be obtained only by measuring the concentration of reactants and/or products in the course of the reaction. The results of these measurements appeared to be correlated with calorimetric data. By way of example, we demonstrate, in Fig. 4, the correlation between the integral heat of reaction and spectrophotometric Cu(OH)(CH₃COO) concentrations in solution for copper powder that was milled for 5 min. Similar correlations are observed for all of the samples examined. Thus, we found that milling changes the reactivity of copper powder toward acetic acid.

To determine the contribution of lattice microdistortions to the heat of the milled copper powder–acetic acid reaction, we characterized the original and milled copper powders by X-ray diffraction using synchrotron radiation. It was found that reflection intensity decreases as the milling time is lengthened. Moreover, milling changes the unit cell parameter of copper (Fig. 5).

Note that the correlation between the 111 interplanar spacing (determined by X-ray diffraction using CuK α radiation) and milling time, which was established in an earlier study, was not confirmed by later data [19]. For this reason, we believe that energy accumulation is not due exclusively to the dislocations mechanically induced in the copper lattice. This view is indirectly supported by the heat of the reaction between milled copper powder and acetic acid: the increase in the heat of this reaction to 45 kcal/mol cannot be due to lattice disordering alone.

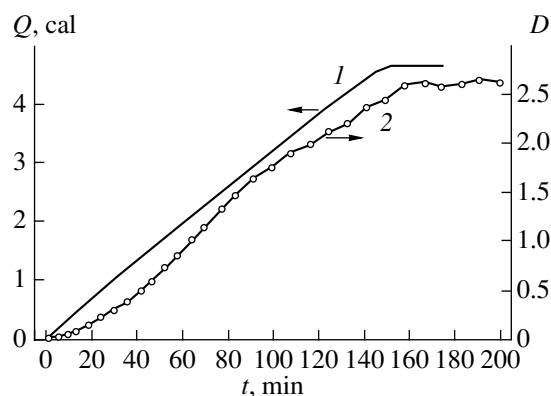


Fig. 4. Variation of (1) the integral heat of reaction and (2) spectrophotometric Cu(OH)(CH₃COO) concentration in the reaction between acetic acid and copper powder milled for 5 min.

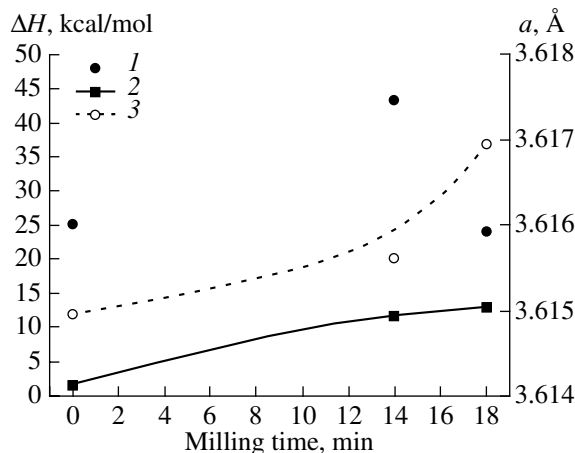


Fig. 5. (1) Heat of the copper–acetic acid reaction, (2) half-width of the 200 reflection, and (3) unit cell parameter a for copper powders milled for 0, 14, and 18 min.

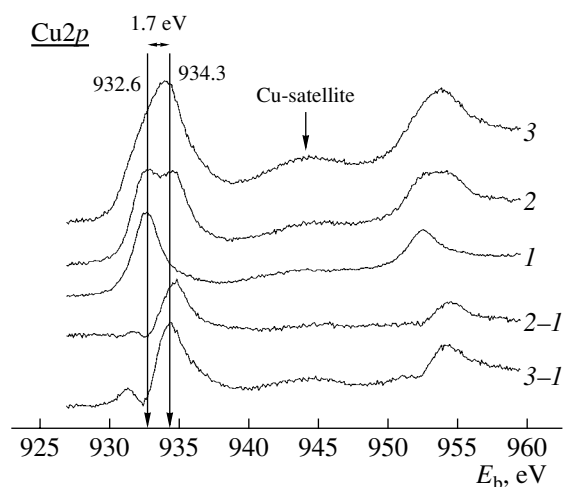


Fig. 6. $\text{Cu}2p$ XPS lines for (1) the initial copper powder and (2, 3) the same powder milled for (2) 14 min (Cu-14M) and (3) 18 min (Cu-18M). (2-1, 3-1) Difference $\text{Cu}2p$ spectra of Cu-14M and Cu-18M, respectively, relative to the spectrum of the initial powder.

Based on the model of crystal nanostructure formation in mechanically activated metals and alloys [22], we assume that the thin amorphous layer that forms at nanograin boundaries as a result of dislocation outcrop upon milling can bind oxygen atoms present on the particle surface or atmospheric oxygen to yield metastable copper–oxygen phases such as Cu_4O and/or Cu_8O [23–25]. A distinctive feature of copper–oxygen solid solutions is that they can reversibly change their stoichiometry in a wide range, the highest reactivity being observed for intermediate compositions [26]. Therefore, the energy delivered by the mechanical activator is accumulated through the formation of energy-rich copper–oxygen compounds on the surface.

To verify this assumption, we carried out an XPS study of the initial copper powder (Cu-ini) and of the copper specimens that were milled for 14 min (Cu-14M) and 18 min (Cu-18M). Lines characteristic of copper, oxygen, and carbon were observed for all specimens. Weak lines due to silicon ($\text{Si}2p$ and $\text{Si}2s$) were also observed for powders that were not ion-sputtered. No lines assignable to other impurities were observed. After ion sputtering, the full-range spectrum showed markedly reduced $\text{C}1s$ and $\text{O}1s$ peaks, much stronger peaks due to copper, and no peaks due to silicon.

According to XPS data, most of the copper in Cu-ini and Cu-14M (Fig. 6, curves 1, 2) is in the Cu^+ state. This is evident from the $\text{Cu}2p_{3/2}$ binding energy (932.6 eV) and from the kinetic energy at which the CuLMM Auger line occurs (916.7 eV). In Cu-18M (Fig. 6, curve 3), copper is in the Cu^+ and Cu^{2+} states. The presence of Cu^+ is indicated by the CuLMM Auger energy ($E_{\text{kin}} = 916.7$ eV), and the presence of Cu^{2+} is evident from a shake-up satellite with $E_b \sim 944$ eV accompanying the $\text{Cu}2p$ peak.

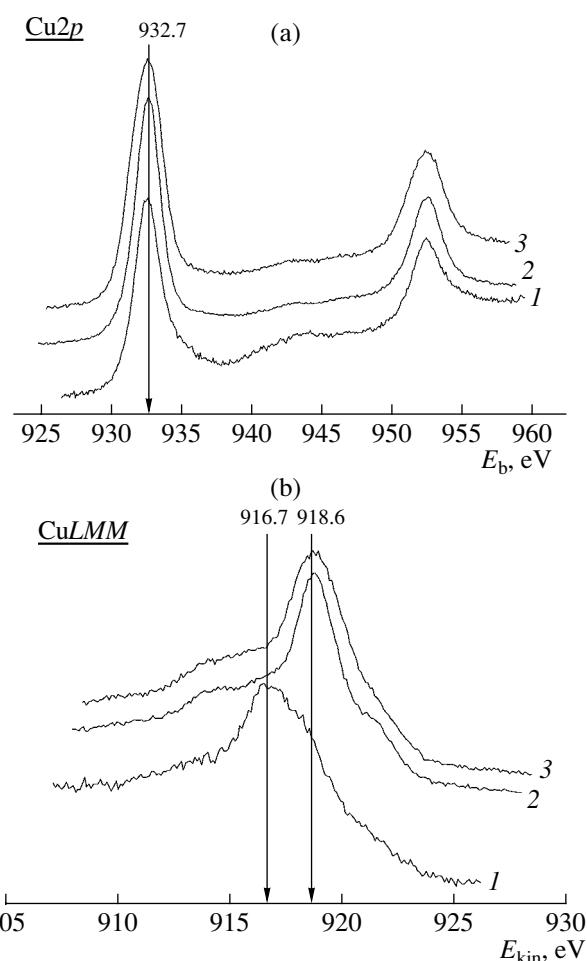


Fig. 7. (a) $\text{Cu}2p$ XPS (b) CuLMM Auger lines for (1) an unspun powder and (2, 3) the same powder ion-sputtered for (2) 1 and (3) 5 min.

Note the unusual shape of the $\text{Cu}2p$ line for unspun Cu-14M and Cu-18M (Fig. 6, curves 2, 3). This line consists of two peaks with $E_b = 932.6$ and 934.3 eV. This splitting may arise from the differential charging of the sample due to the presence of both conducting and nonconducting phases [27, 28]. This effect is particularly evident from the difference spectra (Fig. 6, curves 2-1, 3-1).

After argon ion sputtering for 1 min, copper in all samples is in the metallic state, as is indicated by the $\text{Cu}2p_{3/2}$ binding energy ($E_b = 932.7$ eV) and by the kinetic energy ($E_{\text{kin}} = 918.6$ eV) and shape of the CuLMM Auger line. By way of example, we present, in Fig. 7, the $\text{Cu}2p$ and CuLMM Auger lines for an unspun Cu-ini sample and for the same sample after ion sputtering. Similar results are obtained for the other powders examined.

The above data suggest that the surface of original samples is covered by a copper oxide layer $\sim 1\text{--}2$ nm in thickness, which can be removed by argon ion sputter-

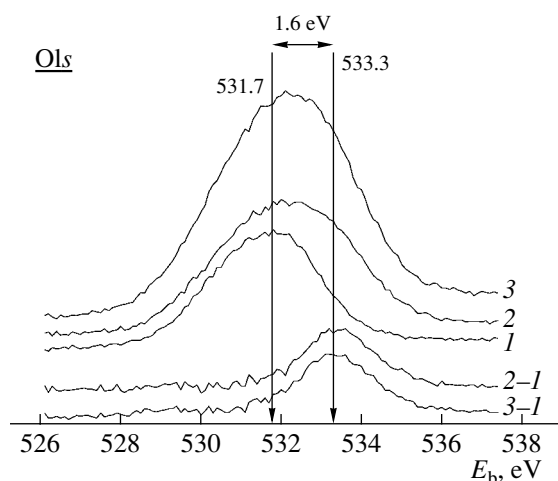
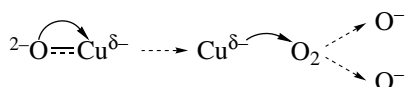


Fig. 8. O 1s XPS lines for (1) the initial ultrafine copper powder and (2, 3) the same powder milled for (2) 14 min (Cu-14M) and (3) 18 min (Cu-18M). (2-1, 3-1) Difference O 1s spectra of Cu-14M and Cu-18M, respectively, relative to the spectrum of the initial powder.

ing for 1 min. In deeper layers, copper is in the metallic state.

The C1s and O1s lines of the original samples are difficult to analyze, because the surface of these samples is contaminated as a result of milling. The spectrum of Cu-ini exhibits a narrow symmetric C1s peak at $E_b = 284.8$ eV. This binding energy is typical of hydrocarbons, which probably come as oil vapor from the diffusion pump. For Cu-14M and Cu-18M, the C1s and O1s peaks are doublets. This splitting can be due to differential charging, as in the case of the Cu2p line.

After ion sputtering for 1 min, the O1s spectrum shows a much weaker narrow peak at $E_b = 530.9$ –531.1 eV. The higher the reactivity of the copper powder toward acetic acid the larger the E_b value at which this peak occurs (Fig. 8). An O1s peak at the same E_b was also observed for polycrystalline copper foil activated with an oxygen–methanol mixture in a study of the catalytic selective oxidation of methanol into formaldehyde [29]. Since this binding energy is typical for neither adsorbed oxygen atoms nor copper oxides, we assign this peak to lattice (suboxide) oxygen bonded with defect sites of the copper polycrystal or powder [30]. Since the XPS peaks of this lattice oxygen are shifted to higher binding energies relative to the peaks of CuO and Cu₂O, the bond between a copper atom and lattice oxygen is covalent to a considerable extent. Therefore, the active sites in copper activated either by milling or by exposure to a reactive medium producing lattice oxygen are oxygen atoms covalently bonded to copper atoms. Based on these considerations, we suggest the following model for the interaction between an active site and an oxygen molecule:



Because of the covalence of its bonds, lattice oxygen donates excess electron density to a neighboring copper atom, whose charge is transferred to a surface atom. The excess electron density on surface atoms activates dioxygen to form very reactive oxygen species (O^-), which then oxidize surface copper atoms. The copper oxides resulting from this reaction react with acetic acids. When activated copper is used as the catalyst in the selective oxidation of methanol into formaldehyde, the reactive oxygen species oxidize methanol molecules. Note that this mechanism is not exhaustive and only gives a general idea of the effect of lattice oxygen on the reactivity and catalytic properties of copper.

A reactive medium can cause profound changes in a catalyst [31–33]. For example, it is believed that, in the selective oxidation of methanol on copper, adsorbed oxygen species responsible for the activity of copper are formed only when the catalytic reaction takes place and are a dynamic system existing only in contact with the reaction medium [29]. In view of this, we believe that, when adsorbed on activated copper surface, some organic compounds, including methanol and acetic acid, favor the shift of electron density to surface copper atoms.

Based on the above mechanism of the effect of lattice oxygen on the reactivity of copper, one can understand why the milling of copper increases the heat of the copper–acetic acid reaction. The overall heat of this reaction is the sum of the heats of the following four processes: acetic acid adsorption on copper surface, electron transfer from surface copper atoms to dioxygen, oxidation of copper by active oxygen species, and copper oxide–acetic acid reaction. While the heats of the third and fourth steps are independent of the sample preparation procedure, the heats of the first and second steps are determined by the way the sample was pretreated. The contribution from the first process to the overall heat of reaction is determined by the surface area of the copper powder. However, very different heats of copper–acetic acid reaction may be observed for copper powders milled for different periods of time and nevertheless having nearly equal specific surface areas [19].

Thus, the key factor in the reactivity of copper toward acetic acid is the presence of lattice oxygen characterized by a higher electron binding energy than Cu₂O or CuO.

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