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Reduction of copper from oxides when heated in air

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The paper presents the results of experiments on the reduction of copper oxides formed during the heat treatment of metallic copper samples in air. The necessary condition is the presence of a muffle made of a material with a higher electron affinity (lower standard electrode potential) compared to copper. Replacing nitrogen in the composition of the atmosphere with an equal proportion of argon does not change the observed redox pattern. Our results indicate an electrochemical mechanism for the reduction of copper oxides in a steel muffle, in which oxygen plays the role of a charge carrier.

Keywords: oxidation of metallic copper, reduction of copper oxides, steel muffle, air, oxygen, electrochemistry.

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The modern concepts of the oxidation mechanism unambiguously stipulate that in the presence of oxygen and other oxidizing gases (H_2O, CO_2, SO_2) there always exist conditions for high-temperature oxidation of metals [1,2]. Therefore, most metals occur in nature in the form of compounds: oxides, chalcogenides, silicates. The main methods for protecting metals against oxidation during heating is heat treatment in inert gases (nitrogen, argon, etc.), in reducing media (CO, H_2, etc.) and in vacuum, and also the use of protective technological coatings (glass enamel, etc.). The latter one makes the heat treatment process much more complicated and expensive. On the other hand, reduction of metal oxides in low-temperature plasma needs high temperatures (4000−5000 K) [3]. However, it was noticed that a number of oxides get reduced when being heated in air [4–6].

This paper presents the results of experiments on reducing copper oxides during heat treatment of metallic copper samples in air in a steel muffle. Our results evidence for an electrochemical mechanism of copper oxides reduction, in which oxygen plays the role of a charge carrier in gaseous electrolyte.

As research samples, specimens of metallic copper in the form of tubes with the outer/inner diameters of 10/8 mm for the electrometric measurements and in the form of rectangular plates $20 \times 16 \times 1$ mm in size for the thermal-gravimetric measurements were used. A tube was installed coaxially inside an open steel muffle having tubular cross-section 18 mm in diameter and wall thickness of 2 mm (low-carbon steel 20, GOST 1050−88) with the aid of bushings made from porous corundum ceramics. In its turn, the muffle was placed into a ceramic tubular heater whose temperature was controlled with a calibrated thermocouple mounted in the middle of the heater (see Fig. 1, *a*). For the electrometric measurements, shielded copper wires in Teflon sheath were attached by spot welding to the outer edges of the copper tube and steel muffle. For the electrometric measurements, shielded Teflon-covered copper wires were attached by spot welding to the outer edges of the copper tube and steel muffle. Microvoltmeter B3-57 was connected to the circuit via electrometric amplifier U5-11 with the input resistance above $10^{15}\,\Omega$. To suppress electromagnetic interference, shields of the connection wires were connected to the common „earth", and the system as a whole was installed in a „Faraday cage" designed as a wooden frame upholstered with an earthed copper grid with the mesh size of about 1 mm.

The defatted copper tube was heated in the open steel muffle to 900°C and then left for cooling in the furnace together with the muffle. The result is visually presented in Fig. 1, *b*. The photo shows that the central segment of the copper tube annealed at the maximal temperature looks like a non-oxidized red copper, while the tube ends that have not been heated to the maximal temperature are covered with a layer of black copper oxide.

Fig. 2, *a* demonstrates the temperature dependence of voltage (difference of potential between the copper tubes and earthed steel muffle). The figure shows that at the temperatures below $\sim 615 \pm 5^\circ$C the copper tube potential is negative, which indicates that its surface is oxidized. However, when the temperature continues increasing, the potential becomes positive (as per definitions used in electrochemistry, the copper tube becomes a cathode); this evidences for the reduction of copper oxides formed earlier on the tube surface. It is extremely improbable that the temperature dependence of thermoelectric difference of potentials at the point where the copper wire is welded to the steel tube is non-monotonic [7,8]. Quasilinear thermo-emf dependence on temperature can only displace the point of zero-voltage temperature relative to the true point of mutual compensation of the redox potentials; in its turn,

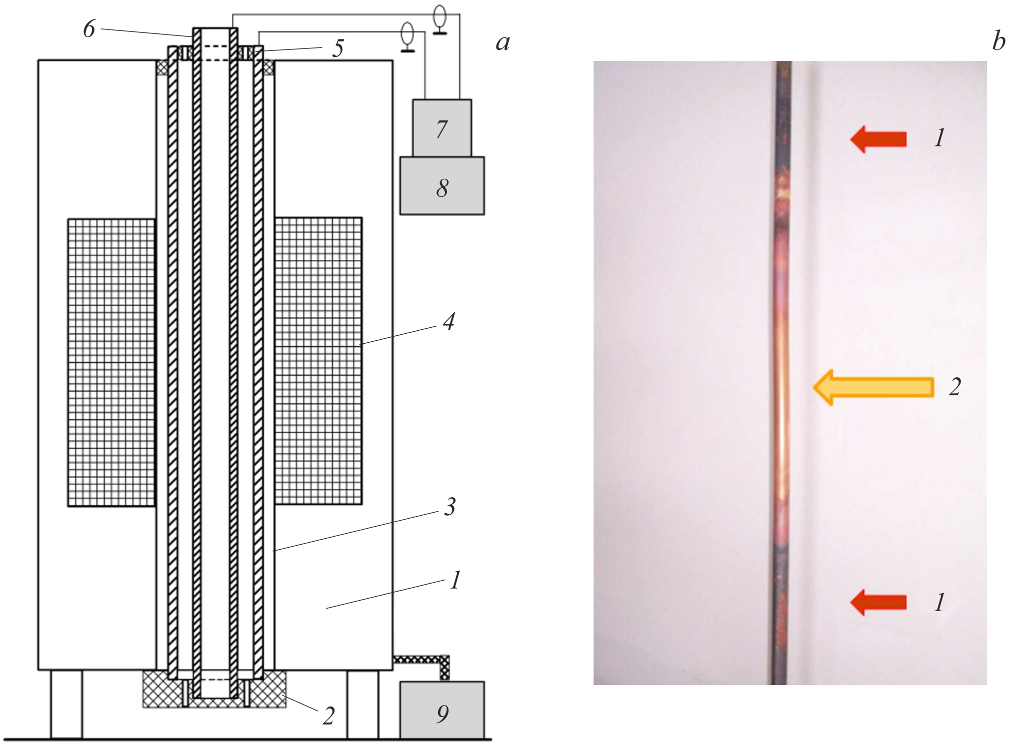

Figure 1. *a* layout of the experimental setup for electrometric measurements: *1* — tube furnace SUOL-0.25.1/12-I1, *2* — ceramic seals, *3* — inner surface of the furnace tubular channel, *4* — heater, *5* — steel tubular muffle, *6* — sample (copper tube), *7* — electrometric amplifier U5-11, *8* — microvoltmeter, *9* — power and temperature controller. *b* — a photo of the copper tube after heat treatment: *1* — oxidized surface areas, *2* — reduced surface area.

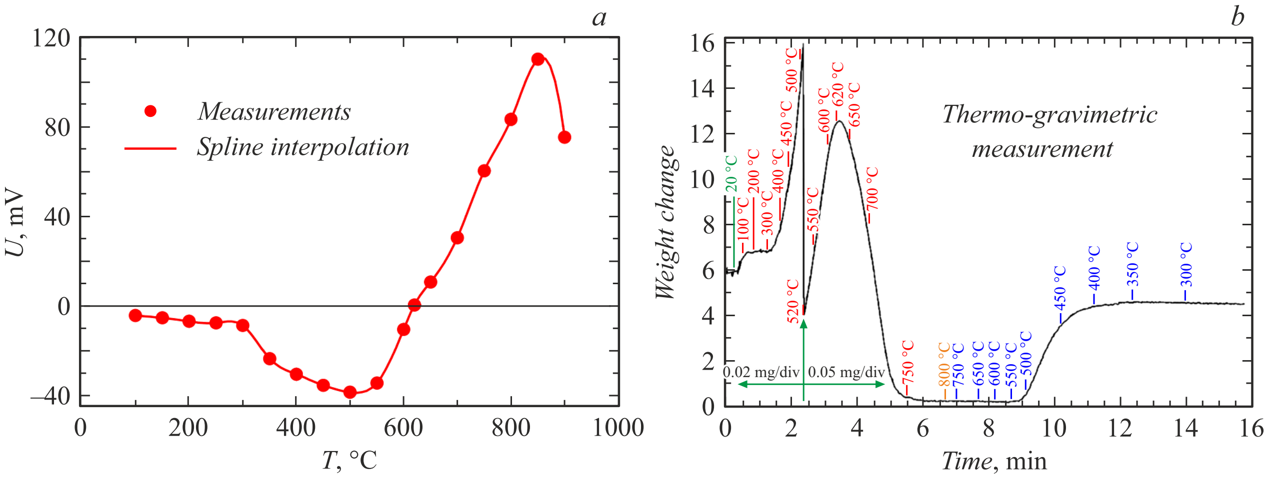

Figure 2. *a* — difference of the copper tube and steel muffle potentials versus temperature. *b* — variation in the copper plate weight in the heating–cooling cycle. The data were recorded in the time-linear mode. During heating to 500°C, the scale division was 0.02 mg; that in the temperature interval from above 500°C (after shifting the recording pen to a new position and changing the scale) to the end of measurements was 0.05 mg.

the point position depends on the temperature distribution over the sample length (Fig. 1).

Defatted copper plates were hung up by a quartz fiber from balance EM-5 so that they were located in the middle of the steel muffle (Fig. 1). The measurements showed (Fig. 2, *b*) that at the beginning of heating the plate weight increases. Then, when the temperature increases to above $\sim 615 \pm 5$°C, the copper plate weight begins decreasing to values below the initial one and reaches a plateau. During cooling in the muffle to below $\sim$ 500°C, the plate weight begins increasing again and reaches another plateau. Bright copper color (see the example in Fig. 1, *b*) indicates low

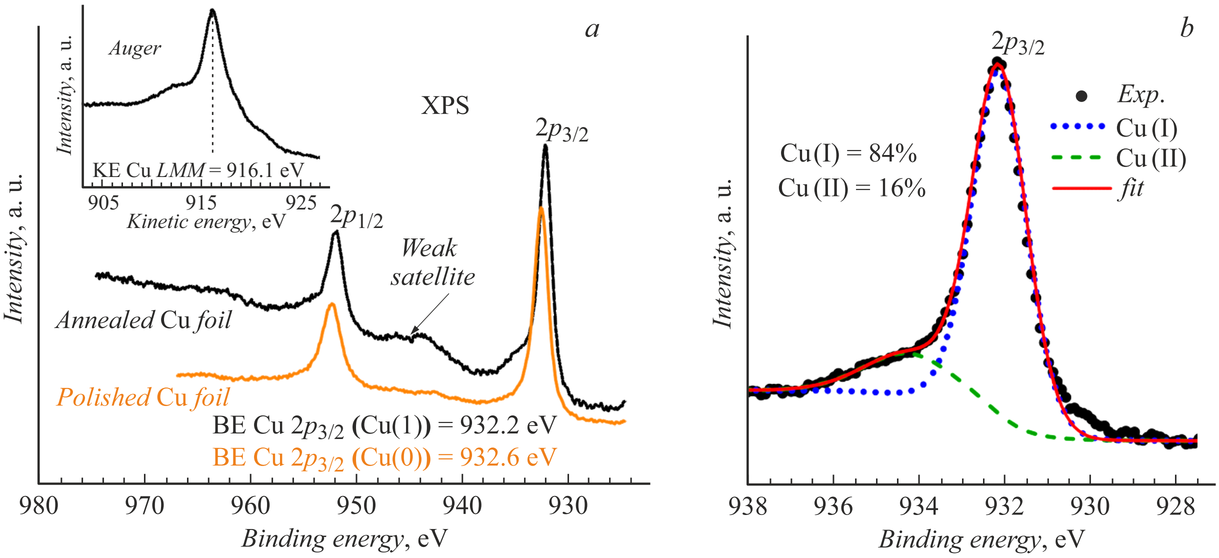

Figure 3. *a* — XPS spectra of the copper plate polished surface prior to and after annealing in the steel muffle. The inset presents the Auger-line $L_3M_{45}M_{45}$ (*Auger*) of the annealed sample. Decomposition of the $2p_{3/2}$-line into valence components.

thickness of the possible surface oxide layer. Fig. 3, *a* demonstrates XPS spectra of the copper plate surface immediately after it has been mechanically polished and defatted and after the cycle of heating–cooling in the steel muffle. Comparison with reference spectra of metallic copper Cu(0) and its oxidized states Cu(I) and Cu(II) [9] shows that the spectrum of the as-cleaned surface is very close to that of metallic copper (the peak $2p_{3/2}$ binding energy is 932.6 eV). The spectrum of the annealed sample consists of intense signal Cu(I) from copper protoxide Cu_2O, on which weak signal Cu(II) from copper oxide CuO is superposed; this is evidenced by the line $2p_{3/2}$ decomposition into contributions of signals Cu(I) and Cu(II) with binding energies of 932.2 and 934.4 eV, respectively (see Fig. 3, *b*) and also by weak satellites in the energy ranges of $\sim 941.5-947.5$ and $\sim 960-965$ eV (see Fig. 4 from [10]). One more evidence of the signal Cu(I) predominance is the modified Auger-parameter $\alpha(\mathrm{Cu(I)}) \cong 1848.3$ eV that is a sum of the Auger-electron kinetic energy 916.1 eV (see the inset of Fig. 3, *a*)) and $2p_{3/2}$-electron binding energy 932.2 eV (compare with $\alpha\big(\mathrm{Cu(0)}\big) = 1851.24$ eV and $\alpha\big(\mathrm{Cu(II)}\big) = 1851.33$ eV, Table 8 in [10]). The fact that the metallic copper signal is not observed in the annealed sample evidences that thickness of the copper protoxide layer is larger than the XPS probing depth (about $4-5$ nm). The copper protoxide is red-colored, contrary to black copper oxide.

Based on the thermal-gravimetric and XPS measurements, we can conclude that the copper plate surface begins oxidizing at the beginning of heat treatment; then (at the temperatures above $\sim 615°$C) there begins reduction of the formed oxides with the loss of the plate weight; finally, during cooling in the steel muffle, the copper plate again gets coated with a dense thin layer of copper protoxide, due to which the plate mass increases.

Since the muffle was open for air inflow from outside, it was important to reveal the roles of the atmosphere components; for this purpose, nitrogen was replaced with argon, i. e. a mixture of 79% of argon (99.9%) and 21% of oxygen (99.9%) was slowly supplied to the sample heating area. The results of thermal-gravimetric measurements appeared to be almost the same as in the case of heating/cooling in atmospheric air. When the steel muffle was replaced with a titanium one, the results also remained the same.

Thus, galvanometric and gravimetric measurements have shown that surfaces of metallic copper samples get oxidized at the temperatures below $\sim 615°$C, while at higher temperatures the oxides on the sample surfaces get reduced to the metallic state. The necessary condition for the reduction is the presence of a muffle made from a metal with high electron affinity (a lower or negative electrochemical (standard electrode) potential, for instance, -0.440 V for Fe^{2+} and -0.037 V for Fe^{3+} as compared with $+0.337$ V for Cu^{2+} [11]). Replacement of nitrogen with argon in the gaseous atmosphere allowed revealing the fundamental role of the atmospheric oxygen as a charge carrier in the redox processes taking place during heat treatment. The similarity with the galvanic element with respect to the potential difference polarity and direction of the redox reaction (reduction of copper) allows concluding that, at the temperatures above $\sim 615°$C, the role of the charge carrier in the gaseous electrolyte is played by ionized molecules of atmospheric air. Thus, the copper electrode gets reduced in the presence of a muffle made from a more electroactive metal despite that heat treatment is performed in air. The described process can find a lot of applications in metallurgy, e. g. for protection against high-temperature corrosion or performing non-oxidizing or reducing heat treatment without using protective or reducing media.

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Conflict of interests

The authors declare that they have no conflict of interests.

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