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INFLUENCE OF TEMPERATURE-TIME HEAT TREATMENT REGIMES ON OPERATING CHARACTERISTICS OF OXIDE FILMS AS APPLIED TO COPPER CAPILLARY-POROUS STRUCTURES

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Temperature-time regimes of heat treatment for producing oxide films on copper capillary-porous structures (CPSs) are determined. The stability of the produced oxide films to multiple heating-cooling cycles under the conditions of the operation of evaporation-condensation systems (ECSs) is shown.

Wetting of the surface of different CPSs (sintered metallic fibers, powders, nets, etc.) by liquid heat-transfer agents is an important factor that contributes to the improvement of their transport characteristics and correspondingly an increase in the efficiency of ECSs operating in a closed-circuit system (heat pipes, steam chambers, heat-exchange surfaces, etc.). One of the methods to improve wettability in a heterogeneous CPS metal–liquid system is increasing the work done by adhesion through the formation of an oxide film on the metal surface [1]. However under conditions of ECS operation that are characterized by heat and mass transfer at high temperatures and pressures as well as multiple heating-cooling cycles, fracture and peeling of the oxide films is often noted. In a CPS with low porosity ($\Pi \leq 0.5$), the flow section of the pores is gradually closed by oxide particles, which impairs the capillary-transport characteristics of the CPS and simultaneously increases the resistance exhibited by a porous layer to a vapor that is generated in it.

Therefore it is a topical problem to produce on CPSs oxide films that have the required service properties (preservation of the initial continuity and the absence of fracture during prolonged periods of operation) and to determine the temperature-time regimes of the technological process of oxidation for their production.

In spite of the promising nature of similar investigations and their practical applicability, there are no experimental data on this problem. The available isolated results [2, 3] were obtained without regard for the influence of the temperature-time regimes of the previous heat treatment on the characteristics of the oxide films, including operating ones, for single values of the temperature and time of oxidation and are of a partial character.

Our work seeks to determine temperature-time regimes for the production of oxide films with the required operating characteristics on the basis of investigating the regularities of copper oxidation in an air atmosphere and to experimentally check the obtained results under near-real conditions of ECS operation. The choice of the material is due to the widespread use of copper as a raw material in manufacturing porous materials.

The oxidation kinetics was studied on specimens of M1 technical copper in a temperature interval of 200 ... 700°C during 1 ... 6 h. The oxidizing medium was air. The specimens were cut out of a stock-produced copper tube and had the following sizes: an outside diameter of 20 mm, a wall thickness of 2 mm, and a height of 15 mm. Prior to oxidation the surface of all the specimens was degreased and etched according to the recommendations [4], and then the initial weight of the specimens was determined using a VLA-1M balance. After these operations the specimens were installed on a substrate, placed in an SNOL-1,6 furnace, heated to the prescribed temperature, and held for the prescribed time. After the completion of the oxidation and the subsequent cooling down to room temperature, a second weighting of the specimens was performed and the change in their weight was calculated from the difference between the initial and final values of the quantities measured. The thickness of the oxide films produced was determined by both calculation and experimental methods on the basis of weight and metallographic (an MIM-7M microscope) analyses. The operating characteristics of the oxide films (continuity, the absence of

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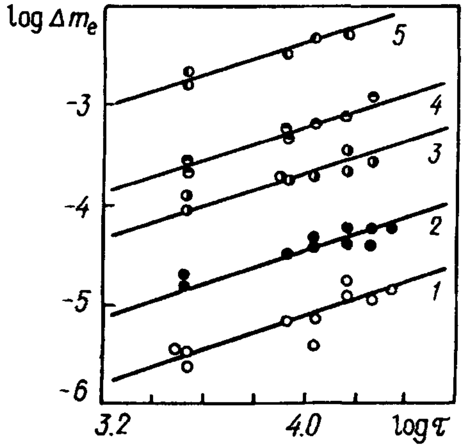


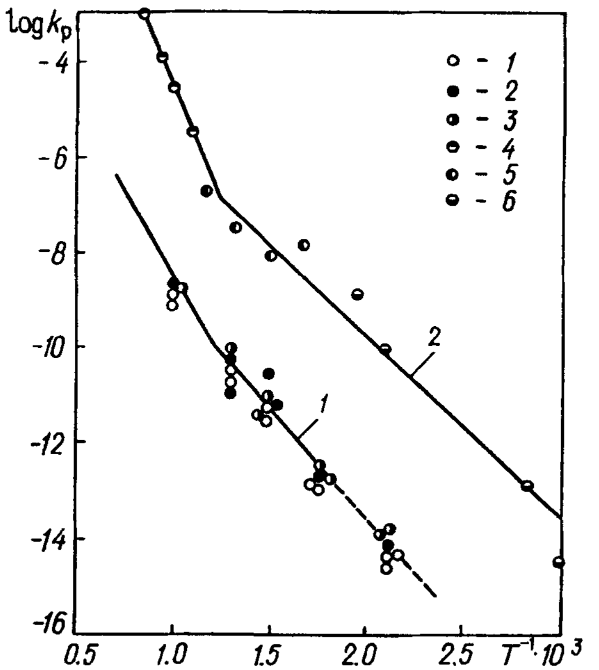


Fig. 1. Increase in the specimen weight versus time: 1) $t = 200^\circ$C, 2) 300, 3) 400, 4) 500, and 5) 700.

Fig. 2. Rate of M1 copper oxidation in air versus temperature: 1) calculated curves [6] and experimental data of the authors (1) τ = 1 h, 2) 2, 3) 4); 2) curves and experimental data [6] (points 4, 5, and 6) for copper oxidation in oxygen. T^{-1}, K^{-1}.

cracking and peeling, strength of the adhesion with a base metal) were assessed visually and using the method of applying a net of scratches [4] after multiple thermal-shock tests of the specimens (heating in the furnace for 3 ... 5 min followed by sudden cooling in water) in the temperature range of 10 ... 250°C.

Analysis of the results of the investigations [5] shows that depending on the conditions of the experiment, particularly, on the temperature and the medium, copper can oxidize by different laws. Therefore the study of the regularities of oxidation and comparison of the obtained results with the data of other works were also among the problems of the present investigation.

The results of measuring the increase in the specimens' weight with time showed that the process of copper oxidation in the studied temperature interval follows a parabolic law (Fig. 1), and the calculated parabolic constants of the oxidation rate k_p are satisfactorily described by the dependences given in [6] (Fig. 2, curves 1):

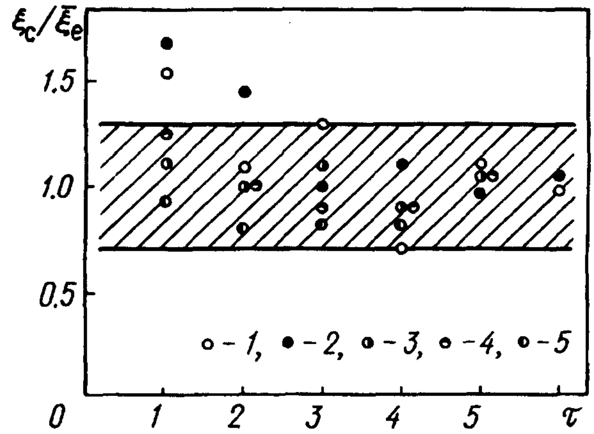
$$k_p = 1.5\cdot10^{-5}\exp[-20140/RT] \quad \text{for} \quad t = 300\ ...\ 500^\circ\text{C}, \tag{1}$$

$$k_p = 0.266\exp[-37700/RT] \quad \text{for} \quad t = 550\ ...\ 900^\circ\text{C}. \tag{2}$$

The results of copper oxidation in oxygen (Fig. 2, curve 2) given for comparison with the data obtained demonstrate that the process of oxidation in both cases is of a self-similar character. However in an oxygen atmosphere, oxidation occurs more intensely as a consequence of the higher content of the oxydizing component.

The thicknesses of the oxide films were determined both experimentally (from the increase in weight) and by a calculation method according to the equations [6]:

$$\xi_e = \frac{\Delta m_e V_{ox}}{M_{O_2}}, \tag{3}$$



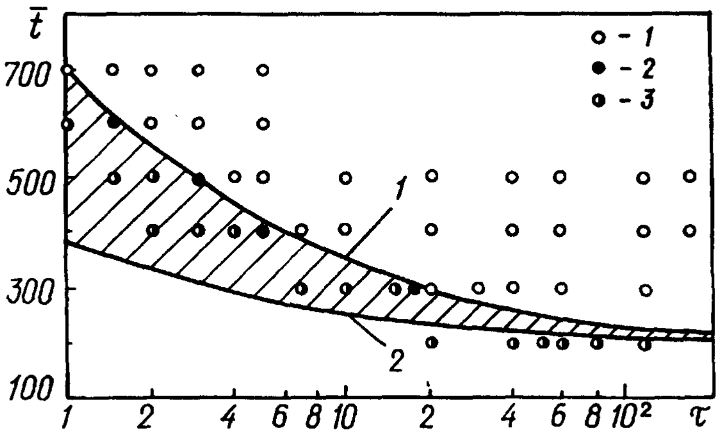


Fig. 3. Comparison of the results of determining oxide-film thickness by calculation and experimental methods: 1) t = 200°C, 2) 300, 3) 404, 5) 500, 5) 700. τ, h.

Fig. 4. Results of investigation of the influence of temperature-time oxidation regimes on operating characteristics of films: 1) complete peeling and fracture of a film; 2) partial peeling (cracking); 3) the absence of cracking or peeling. t, °C; τ, min.

TABLE 1. Comparison of the Thicknesses of Oxide Films Measured by Different Methods

t, °C	τ, h	ε_c, μm	ε_e, μm	ε_m, μm
200	1	$3.91 \cdot 10^{-2}$	$2.25 \cdot 10^{-2}$	$2.52 \cdot 10^{-2}$
300	5	$5.68 \cdot 10^{-1}$	$5.72 \cdot 10^{-1}$	$6.50 \cdot 10^{-1}$
400	1	$9.50 \cdot 10^{-1}$	$8.69 \cdot 10^{-1}$	$7.92 \cdot 10^{-1}$
400	2	1.34	1.35	1.48
700	1	13,67	14.84	13.95

$$\xi_c = \frac{(k_p \tau)^{0.5} V_{ox}}{M_{O_2}}, \tag{4}$$

where V_{ox} is the molecular volume of the copper oxide CuO, which is, according to [5], the main component of the oxide film in the temperature range of 200 ... 700°C for a partial pressure of the oxygen in the air $P_{O_2} = 0.21\ P_{atm}$; M_{O_2} is the atomic weight of the oxygen multiplied by the number of its atoms in the metal oxide.

For a comparative assessment of the results obtained by Eqs. (3) and (4), we also performed sampling measurements of the oxide film thickness on microsections of specimens using a metallographic microscope (see Table 1), the oxide film thickness being determined as the arithmetical mean of 15 measurements of the film thickness on each microsection.

Analysis of the results (Fig. 3, Table 1) shows that all the calculated and experimental magnitudes of the film thicknesses have the same order and a small spread (within the error of the experiment and the methods for determining film thicknesses), and satisfactory agreement of the data obtained by the different methods can be inferred. The difference between the experimental and calculated data in the region of relatively low temperatures ($t \leq 300$°C) in the first hours of oxidation (τ = 1 ... 2 h) is explained by the small thickness of the oxide films and correspondingly the insignificant change in specimen weight. At a later time, as the oxidation time increases, the film thickness grows, approaching the calculated values.

When studying the operating characterisitics of the films, cracking and partial or complete peeling of the scale were noted to occur on some specimens that oxidized at $t \geq 200^{\circ}C$ for $\tau \geq 1$ h even for gradual cooling down to room temperature. This is apparently due to the development of stresses at the oxide layer-metal interface as a consequence of the differences between their coefficients of linear expansion as well as deformations in the oxide layer itself. Allowing for this factor, to determine temperature-time regimes of oxidation that permit the production of films in which the forces of adhesion with the base metal exceed the developing stresses in cooling, we also investigated specimens of the same sizes oxidized in the same temperature range but for shorter periods of time ($1 \leq \tau \leq 60$ min).

Figure 4 presents the results of our investigation that permit establishment of a limit of existence for stable oxide films (curve 1), below which no cracking or peeling was observed. Here, curve 2 was calculated by the authors using Eq. (4) and constructed with allowance made for the data of [1], in which it is noted that wetting of the CPS material by the heat-transfer agent improves when an oxide film thickness within 0.05 ... 0.1 μm is attained. Clearly the region of the existence of oxide films that have a thickness sufficient to increase wettability and the required operating characteristics as applied to the ECS CPSs will be between these two curves.

With the aim of checking this assumption we tested those specimens whose temperature-time regimes of oxidation were in the indicated region for stability to thermal shocks (the number of cycles was equal to 10). The analysis of the results of visual observations of the state of the oxide film surface showed the absence of any fracture. Subsequent experiments using the method of applying a net of scratches to the specimen surface confirmed the validity of the data obtained, too.

Thus, as a result of the performed investigations temperature-time regimes for producing oxide films on CPSs from M1 technical copper in an air medium are determined. The region of the existence of oxide films that are firmly connected to the base metal is established and their stability to multiple heating-cooling cycles under conditions of thermal shocks is shown. The indicated temperature-time regimes for the treatment of technical copper can be recommended for use in producing ECS CPSs as well as other different heat-exchange surfaces, both porous and solid, where high wettability and a long service life are required.

NOTATION

t, T, temperature; k, constant of oxidation rate; R, gas constant; ξ, film thickness; τ, time; Δm, increase in specimen weight; V_{ox}, molecular volume of oxide; M_{O_2}, atomic weight of oxygen; P_{O_2} and P_{atm}, partial pressure of oxygen and atmospheric pressure of air. Subscripts: p, parabolic; e, experimental; c, calculated; m, microscope.

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