

THE EFFECT OF PREPARATION CONDITIONS AND THE IONIZING RADIATION ON THE KINETICS OF CUPRIC OXIDE REDUCTION BY HYDROGEN

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The cupric oxide reduction in the temperature interval 170–350°C has been studied by thermogravimetry. The reduction kinetics can be quantitatively described by the modified Prout–Tompkinson equation, with the apparent activation energy varying within the limits (4.94–5.82) · 10⁴ J/mol. Irregularities observed during the reduction of the oxide of the oxalate origin are due to the high content of the metallic phase. The *p*-semiconducting nature of these oxides has been proved for all samples. The effect of the preirradiation of samples by γ -rays (with the absorbed dose $D_\gamma = (1.4-4.75) \cdot 10^6$ J/kg) on the reduction kinetics depends on the origin of the cupric oxide. In contrast to NiO no correlation between the content of the super-stoichiometric oxygen and the reduction kinetics has been found. After irradiation by an order-of-magnitude-higher dose of γ -rays or by fast neutrons with the dose $D_n = 79.8$ J/kg the reduction rate increases and the activation energy decreases regardless of the oxide origin. At the same time the concentration of the ionic form of the super-stoichiometric oxygen increases.

The kinetics and mechanism of the cupric oxide reduction by hydrogen has been studied by many authors from various points of view¹⁻³. Kurchatov and coworkers^{4,5} found a strongly exothermic nature of this reaction, causing a specific shape of the kinetic curves observed at lower temperatures of the reduction. The local overheating of the oxide and the formation of dislocations in tablets of CuO can be the reason of the so-called reversed reduction profile, *i.e.*, when the reduction proceeds from the center towards the surface of the sample. The autocatalytic mechanism of the cupric oxide reduction has been proved already earlier⁶ but the positive effect of copper, that activates the reducing gas, was partly recognized only in the more recent studies⁷⁻⁹. Various results in the published literature are presented in connection with the retarding effect of water vapour on the reduction kinetics^{2,10}. A relatively low attention has been paid to the effect of the genesis and preparation conditions on the cupric oxide reduction. Bond¹¹ observed various initial reaction rates using cupric oxides obtained by the decomposition of the hydroxide, nitrate, or by the oxidation of compact copper wires.

In this study we concentrated our effort to the study of the dependence of the cupric oxide reduction kinetics on the origin of the oxide and on the effect of preirradiation of the oxide by γ rays and fast neutrons.

EXPERIMENTAL

The cupric oxide of the nitrate origin has been prepared from the cupric nitrate of analytical grade purity (Lachema) by decomposing it for 3 hours on the air at 300°C. The cupric oxide

of the carbonate origin has been prepared by calcination of commercial carbonate (Lachema, analytical grade) for 3 hours at 400°C. A part of the carbonate sample was calcinated on the air, another one in nitrogen under the same conditions. After the decomposition the formed oxide was kept in the nitrogen atmosphere until it cooled down to the room temperature. The cupric oxide of the hydroxide origin has been prepared by precipitation from the saturated aqueous solution of cupric nitrate by the solution of sodium hydroxide at 0°C. The suspension of the precipitated cupric hydroxide has been decomposed by boiling for 1 hour. The formed oxide was repeatedly washed by distilled water and by ethanol and dried at the room temperature. The cupric oxide of the oxalate origin has been prepared from the solution of cupric nitrate (1 mol/l) by precipitation using a potassium oxalate solution of the same concentration. A part of the precipitate, dried at the room temperature, was calcinated on air at 350°C, another part in the nitrogen atmosphere. Before the analysis both samples were washed by the hydrochloric acid (10^{-3} mol/l) to remove the non-decomposed oxalates.

From all samples a fraction with the grain size within 0.05–0.2 mm has been separated by sieves and used in the subsequent experiments. The content of copper has been determined by electroanalysis. The specific surfaces of the samples have been measured by the adsorption of nitrogen at low temperatures. The fine structure has been determined by the Debye-Scherrer method. The content of the super-stoichiometric oxygen was determined by iodometry¹². The notation, composition, and other parameters of samples are summarized in Table I.

The individual samples were divided into several portions. Some of them were irradiated by the cobalt γ rays by various doses ranging from 1.4 to 4.75 $\cdot 10^6$ J/kg. Other were irradiated over a long period of time so that the total absorbed dose reached the value of 1.4 $\cdot 10^7$ J/kg. Still other samples of the oxide were irradiated by fast neutrons from the Am-Be source in two irradiation experiments with the neutron flux density 2.39 $\cdot 10^{16}$ n/m² and 4.45 $\cdot 10^{16}$ n/m² (the absorbed doses were $D_n = 42.8$ and 79.8 J/kg, respectively). The reduction reaction was followed in the temperature range 170–350°C under the identical experimental conditions for the original oxides and for the samples treated by radiation as described.

The reduction kinetics has been followed by thermogravimetry using an apparatus described in the paper¹³. Using samples of the weight of 50 mg and the hydrogen flow of 56 ml/min the resulting values of the rate and their time dependences are independent of these parameters.

RESULTS

Physico-Chemical Properties and Parameters of the Cupric Oxide of Various Origin

The results of the chemical analysis (Table I) and of the X-ray diffraction experiments show that the samples of the oxalate origin contain (along with the cupric oxide) various amounts of elementary copper, depending on the composition of the atmosphere during the decomposition. Assuming that the system is composed only of copper and oxygen (Table I) the sample No 5 contains 66.9 wt.% of CuO and the sample No 6 91.6 wt.% of CuO. The specific surface area changes with the origin of the sample within practically two orders of magnitude. The low values of the surfaces of oxides of the nitrate and oxalate origin agree with the published data¹¹ and they are caused by the different conditions of their population, including the atmosphere during the decomposition of the original salt and also by the surface areas of these salts¹⁴.

The microscopic examination, both by the optical and electron microscopes, revealed that these factors influence directly the morphology, dispersion and the aggregation degree of the individual elementary crystals, determining thus the surface area of the resulting oxide.

From the data of Table II it follows that the samples of various origin are differently sensitive towards the thermal treatment and the sintering processes. The relatively smallest change of the surface area of the oxalate-origin oxide, treated at 600°C, is probably due to the presence of the dispersed metallic copper that can play a role of a stabilizing carrier suppressing the sintering processes. The irradiation of oxides by γ rays or neutrons has no effect on their surface areas.

Various preparation conditions, namely the atmosphere during calcination, are reflected in the amount of the adsorbed super-stoichiometric oxygen. The cupric

TABLE I

Notation, Composition, Specific Surfaces S and the Content of the Super-stoichiometric Oxygen in Cupric Oxide of Various Origin

Sample	Wt.% Cu	Wt.% CuO	S m^2/g	Super-stoichiometric oxygen		Origin calcination atmosphere
				wt.%	mg/m^2	
1	78.15	97.82	12.57	0.008	0.006	CO_3^{2-}/N_2
2	78.16	97.84	9.40	0.061	0.065	CO_3^{2-}/air
3	79.70	99.76	0.29	0.017	0.586	NO_3^-/air
4	77.35	96.83	20.70	0.015	0.007	OH^- in solution
5	86.56	108.20	2.07	0.020	0.097	oxalate/air
6	81.58	101.97	0.67	0.020	0.297	oxalate/ N_2

TABLE II

Specific Surfaces of the Original Samples of CuO (m^2/g) and of the Same Samples Treated for 60 min at Various Temperatures in the Nitrogen Atmosphere

Sample	2	3	4	5
Untreated	9.40	0.29	20.70	2.07
Treated at 500°C	7.82	0.26	11.02	1.76
at 600°C	4.75	0.09	2.59	1.18

oxide of the carbonate origin contains an order-of-magnitude-higher absolute amount of oxygen (relatively to the surface area unit) if compared with the same sample prepared by calcination in an inert atmosphere (Table I). The low oxygen concentration in the sample No 4 corresponds to its preparation method because this sample has never been exposed to the atmospheric oxygen. In oxides of the oxalate origin (samples No 5 and 6) the presence of the metallic phase causes probably a shift of the $\text{Cu}^{2+}-\text{Cu}^{3+}$ equilibrium towards the formation of Cu^{2+} ions. The equilibrium concentration of Cu^{3+} ions (and the corresponding equivalent concentration of the ionic form of oxygen) is thus lower in the sample No 5 (calcination on the air), because this oxide contains approximately 4 times more of copper than the sample No 6. The irradiation of oxides by γ rays with doses ranging from 1.4 to $4.75 \cdot 10^6$ J/kg does not change the concentration of the super-stoichiometric oxygen. Only the higher dose ($D_\gamma = 10^7$ J/kg) the concentration of the ionic form of oxygen increases by nearly one order of magnitude, depending on the origin of the oxide. Similarly, the irradiation by fast neutrons increases the concentration of the super-stoichiometric oxygen. At the dose $D_n = 42.8$ J/kg only a negligible increase of the oxygen concentration has been observed but at the dose $D_n = 79.8$ J/kg this concentration increases 2–16 times, depending on the sample origin.

Reduction of Oxides

In the region of low reduction temperatures ($170-230^\circ\text{C}$) the exothermic nature of the reaction is strongly emphasized. During the induction period and during the initial stage of the process the sample is being locally overheated (the measured increase of the bed temperature amounted up to 50°C) and the reaction rate reached practically immediately its maximum values. The reduction was therefore studied only at higher temperatures of $230-350^\circ\text{C}$. The reduction kinetics can be quantitatively described, regardless of the sample origin, by the Prout-Tompkinson equation modified by Bond¹¹

$$\log [(x + \alpha)/(1 - \alpha)] = k \cdot t, \quad (1)$$

where α is the reduction degree in the time t and the constant $x = 0.3$ under the assumption that the reaction reaches its maximum rate at the reduction degree $\alpha = 0.3$. The reaction rate constants k were determined from the slopes of the linear parts of the function $\log [(0.3 + \alpha)/(1 - \alpha)] = f(t)$. The highest rate constant (Fig. 1) has the reduction of the oxide of the hydroxide origin, the reduction of the samples of the carbonate origin is slower, the reduction of the nitrate-origin oxide is still slower, and the slowest reduction has been found for the oxide prepared by the decomposition of the oxalate in the nitrogen atmosphere. The values of the apparent activation energy of reduction (Table III) lie within $(4.94-5.82) \cdot 10^4$ J/mol, which agrees with the published data^{4,5,11}. The effect of the gaseous atmosphere

of preparation has been observed for samples of the oxalate origin which thus make an exception from this point of view. The sample prepared by the decomposition on air has a high reduction rate at lower temperatures so that this rate at 260°C is comparable with the reduction rate of the carbonate-origin oxide (Fig. 1). At higher temperatures this rate is evidently limited by the internal transport processes which follows also from the magnitude of the activation energy.

The oxidation kinetics of the primarily reduced oxide and the subsequent secondary reduction has been studied so that the standard weight of the sample was, after the first reduction, oxidized at the same temperature by a stream of dry air up to the constant weight increase. Then hydrogen has been introduced into the reaction vessel and the sample was again reduced (Fig. 2). During the experiment time no 100% oxidation has been observed. The secondary reduction proceeds faster than the primary process and all the oxide formed by the oxidation of the metal has been reduced. The oxidation degree and therefore also the secondary reduction increases with the increasing specific area of the initial samples. The oxides formed by the oxidation of the metal have substantially lower specific surface areas than the original oxides (*e.g.*, the reoxidized sample No 2 has the surface area of 1.70 m²/g in comparison with 9.40 m²/g). Also the amount of the surface super-stoichiometric oxygen is lower in the reoxidized samples (in the sample No 2 it decreased from 0.061 wt.% to 0.00 wt.%). In the debyegramms of reoxidized samples along with all selective reflections of the cupric oxide also the most intense reflections of elementary copper have been observed.

From Fig. 3 it is obvious that the reduction rate is markedly influenced by the irradiation only at high applied doses of γ radiation ($D_\gamma \approx 10^7$ J/kg) or at $D_n = 79.8$ J/kg for the neutron irradiation. Under these conditions the reaction rate

TABLE III

Values of the Apparent Activation Energy of the Reduction of Cupric Oxide of Various Origin ($E_a \cdot 10^4$ J/mol) for the Unirradiated Samples and for Samples Irradiated by γ Rays with a Dose of $2.75 \cdot 10^6$ J/kg and by Fast Neutrons with a Dose of 79.8 J/kg

Sample	1	2	3	4	5		6
					200–260°C	260–320°C	
Unirradiated	5.27	4.94	5.02	5.48	17.91	2.68 ^a	5.82
γ -Irradiated	2.17 ^a	6.45	7.91	8.20	19.13	—	8.01
Irradiated by neutrons	3.05	4.48	4.69	5.36	17.50	—	5.23

^a Kinetics of these reductions lies evidently in the diffusion region.

increases for all samples regardless of their origin. The smallest reaction rate change has been observed for the sample No 6 of the oxalate origin (the rate constant increased by 20% after the γ ray irradiation), the largest change has been observed for the carbonate-origin sample (the rate increased twice). At lower doses of γ radi-

FIG. 1

The Dependence of the Logarithm of the Rate Constant on the Reciprocal Temperature for the Reduction of CuO of Various Origin by Hydrogen

The numbers at curves correspond to the notation of samples as given in Table I.

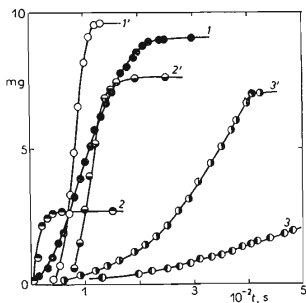
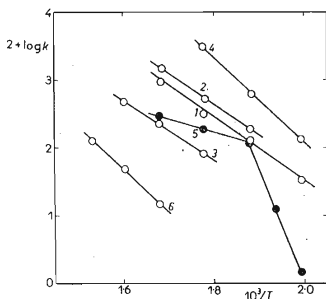


FIG. 2

The Time Dependence of the Primary Reduction, Oxidation, and Secondary Reduction of Samples (Table I) No 3 and 4 (Dashed Curves) at 290°C

1, 1' Primary reduction (the curve is shifted to the coordinate origin); 2, 2' the secondary reduction; 3, 3' oxidation.

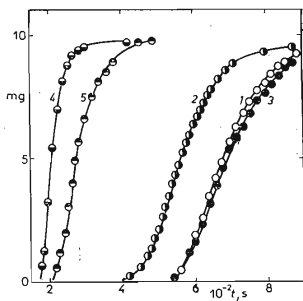


FIG. 3

The Time Dependence of the Reduction of the Sample No 3 at 260°C and of the Same Sample Irradiated by Various Radiations

1 Unirradiated sample; 2 γ -irradiation, dose $4.75 \cdot 10^6$ J/kg; 3 neutron irradiation, dose 42.8 J/kg; 4 neutron irradiation, dose 79.8 J/kg; 5 γ -irradiation, dose $1.4 \cdot 10^7$ J/kg.

tion (in the range $D_\gamma = (1.4-4.75) \cdot 10^6 \text{ J/kg}$) (Fig. 4) the sample No 4, for which the reaction rate increases linearly with the dose, was found to be the most sensitive. On the other hand, in the sample No 6 the rate decreases and at $D = 4.75 \cdot 10^6 \text{ J/kg}$ is only about 15% of the initial value for the unirradiated sample. The reduction rates for the sample No 1 and 3 remain practically unchanged. The neutron irradiation by a dose $D_n = 42.8 \text{ J/kg}$ has practically no effect on the reduction rate.

The values of the apparent activation energies of the reduction of samples (Table III) increased for all samples irradiated by γ rays with a lower applied dose ($D_\gamma = 2.75 \cdot 10^6 \text{ J/kg}$) if compared with the values for non-irradiated oxides. On the other hand, after the neutron irradiation by a dose $D_n = 79.8 \text{ J/kg}$ or after the γ irradiation by a dose $D_\gamma = 10^7 \text{ J/kg}$ that cause an observable increase of the reaction rate, the activation energy of reduction decreases.

DISCUSSION

From the experimental results it follows that the cupric oxide is formed under the conditions used for the preparation and decomposition of various original salts. The samples of the oxalate origin are an exception because a two-component system is formed by the formation of the oxide and elementary copper by the reactions $\text{Cu}(\text{COO})_2 \rightarrow \text{Cu} + 2 \text{CO}_2$ and $\text{Cu}(\text{COO})_2 \rightarrow \text{CuO} + \text{CO} + \text{CO}_2$. Along with these reactions a certain part of cupric oxide might be reduced by carbon monoxide, $\text{CuO} + \text{CO} \rightarrow \text{Cu} + \text{CO}_2$. The degree of decomposition and the dominant role of the individual reactions is a function of the temperature and of the actual partial pressures of the gaseous components. In full agreement with the experimental results (Table I) an effect of the calcination atmosphere on the final composition of the sample and on the ratio $\text{CuO} : \text{Cu}$ can be expected. From the results of the reoxidation experiments it follows that at 260°C and at higher temperatures a relatively

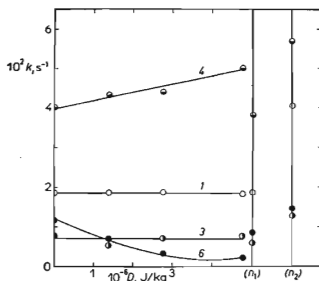


FIG. 4

The Dependence of the Rate Constants of the Reduction of CuO of Various Origin on the Dose of the γ -Radiation and After the Irradiation by Fast Neutrons with Doses 42.8 J/kg (axis n_1) and 79.8 J/kg (axis n_2)

The numbers at curves correspond to the notation of samples as given in Table I; the reduction temperature: 1, 3, 4 260°C ; 6 350°C .

fast oxidation of copper by the air oxygen takes place, but only to a certain degree α_0 . During the oxidation a continuous layer of cupric oxide is formed so that it hinders the gas diffusion towards the metal-oxide interface and therefore also any further oxidation. This fact allows to explain the substantially lower content of CuO in the sample No 5 (calcination on the air) in contrast to sample No 6 (calcination in nitrogen) also by the subsequent mechanism. At 350°C the decomposition of the oxalate proceeds predominantly according to the first equation. In the air atmosphere the formed copper is rapidly oxidized to the oxide the surface layer of which prevents further oxidation of the sample. On the other hand, in the stream of the technical grade nitrogen, which does not guarantee a "pure" inert atmosphere, a slow oxidation proceeds (the decomposition time ~ 3 hours) also in the deep subsurface layers. The content of CuO in this sample will be therefore higher. The control experiments with oxygen-free argon confirmed this assumption.

Semiconductivity of the type, in which the hole- and electron conductivities are in equilibrium, is assumed for cupric oxide¹⁵. However, this type is valid only for the stoichiometric oxide. Either type of conductivity can prevail depending on the conditions of preparation. The experimental data show that there is the super-stoichiometric oxygen in our samples of CuO, the content of which depends on the genesis of the oxide. The experimental results about the type of semiconductivity, determined from the sign of the thermoelectric voltage, agree with this assumption. All the oxides under study behave as *p*-semiconductors. The increase of the concentration of ionic super-stoichiometric oxygen after the γ or neutron irradiation of the sample was also observed and described for nickel oxide¹⁶ irradiated either on air or in vacuum¹⁷. On the basis of these observations it can be assumed that even in cupric oxide the described effect is due only to the shift of the equilibrium of the already present super-stoichiometric oxygen from the neutral towards the ionic form¹⁸. However, in nickel oxide the threshold dose for this transition is about two orders of magnitude lower than in cupric oxide ($D_{\gamma, NiO} = 7 \cdot 10^5 \text{ J/kg}$)¹⁶. This fact may be connected with the relatively higher tension and lability of the surface oxygen in cupric oxide.

From Table III and Fig. 1 it follows that the oxide of the oxalate origin, prepared by the decomposition on air, has an exceptional behaviour. This sample can be characterized by a high reaction rate at lower temperatures (200–260°C), which at higher temperatures is limited by the transport processes. The relatively high value of the apparent activation energy of reduction of this sample is another anomaly. The basic parameter of this sample by which it differs from other samples is the high content of metallic copper present already in the original oxide. The metallic phase has therefore a well developed and sufficiently stable crystalline lattice. It cannot cause any autocatalytic acceleration of the process, *e.g.*, by the activation of adsorbed molecules of the reducing gas by atomization, similarly as it proceeds with a nascent metal produced during the reduction, the catalytic effect of which was

already proved⁹. Because of the preparation conditions we may assume a high dispersion of the metallic copper in the oxide so that every volume element of the sample as well as its surface contain a relatively high concentration of local regions with a metal-oxide interface. The presence of metal in the original oxide affects the equilibrium concentration of its lattice defects, the formation of the contact potential on the phase boundary, and it modifies also the distribution and surface of pores⁷. The change of the geometric and electric properties can primarily cause the change of the adsorption properties of the oxide. Due to the high concentration of the regions of local interfaces the reaction can start simultaneously from many centers and by the same mechanism it can proceed even in the deeper layers of the sample. The high reduction rate of this oxide will thus result. However, the activity of these centers is relatively low as proved by the value of the activation energy. The contact of the thin layer of the metal with cupric oxide can be characterized by the electric double-layer⁷, in which the oxide surface is negatively and the metal positively charged. Because of the donor character of the hydrogen adsorption this interface will constitute a significant potential barrier for the adsorption of its molecules on cupric oxide. The adsorption processes on the interface will then determine also the resulting value of the activation energy which will be relatively high. It is probable that also other factors will participate on the anomalous properties of the sample No 5 during the reduction. Due to the highly exothermic character of the reaction the local overheating of the sample already in the initial stages of the reaction may be the reason of the non-isothermal character of the reaction even at a constant temperature of the external source. The heat transport in the sample material will be speeded up by the presence of the metallic phase. The reaction can be therefore initiated practically simultaneously in several points of the grain because the actual temperature will be in these points higher than the adjusted temperature. These processes lead also to an increase of the reaction rate. Moreover, a parallel reaction cannot be excluded, *e.g.*, the reduction decomposition of small amounts of the non-decomposed salt present in the original oxide. The existence of such a reaction is corroborated by the fact that the basic integral curve of the time dependence of the reduction of oxalate samples has two inflection points corresponding to two maximum rates divided by a short plateau.

According to the published data¹⁹ the initial observable stage of the reduction of certain oxides can be expressed by the equation $\alpha = k \cdot t^n$ where the symbols have the same meaning as in Eq. (1). Also the results of this study can be described by this equation. The slope of the initial linear section is given by the formation of metallic nuclei so that for samples of the identical chemical composition similar dependences $\log \alpha = f[\log(t)]$ can be expected. The values of the exponent n , ranging from 1.7 to 2.1, indicate a two-dimensional nucleation in complete agreement with the results of other authors²⁰.

It follows from the reoxidation experiments that the oxidation of copper, freshly formed by the primary reduction, proceeds also *via* a two-dimensional mechanism which determines the formation of a continuous layer of the oxide. It has been proved experimentally that the oxidation degree α_0 is a function of the specific surface of the original oxide (S), according to the relation: $\alpha_0^2 = k' \cdot S$, where k' is the proportionality constant. At the constant reaction temperature the thickness of the oxide layer is practically identical for all samples which explains the dependence of the achieved oxidation degree α_0 on the specific surface of the metal, eventually the dependence on the specific surface of the original oxide. In cupric oxide we thus observe not only a direct proportionality to the specific surface of the original salt but also in the entire genetic series¹⁴: original salt $\xrightarrow{\text{(calcination)}}$ oxide $\xrightarrow{\text{(reduction)}}$ metal. The secondary reduction proceeds in all samples by the same mechanism as the primary process. However, the rate constants of the secondary reduction are substantially higher because the oxide formed by the oxidation, which is so far not structurally stabilized, exhibits a higher reactivity.

In the region of lower applied doses of γ radiation up to the value $D_\gamma = 4.75 \cdot 10^6$ J/kg the reaction rate in samples of various origin (Fig. 4) changes in a different way (*cf.* samples No 4 and 6, Table I), or no change in the kinetics has been observed at all (samples No 1 and 3). The application of an-order-of-magnitude-higher dose ($D_\gamma \sim 10^7$ J/kg) causes undoubtedly an increase of the reaction rate, regardless of the origin of the oxide. The concentration of the ionic form of the super-stoichiometric oxygen simultaneously increases. The irradiation by fast neutrons by the dose $D_n = 42.8$ J/kg in the first case and $D_n = 79.8$ J/kg in the second case have practically the same result. In our previous study¹⁸ and also in the studies of other authors¹⁶ a distinct correlation between the content of the ionic super-stoichiometric oxygen in nickel oxide and the kinetics of its reduction has been found regardless of the fact whether the changes of the oxygen content were caused by the ionizing radiation, thermal treatment, or by the method of preparation. In agreement with the ideas of the electron theory of adsorption on semiconductors the shift of the equilibrium between various forms of the super-stoichiometric oxygen in favour of the ionic leads to the shift of the position of the Fermi level on the surface of the *p*-semiconductor towards its conductivity band. This leads to a lower adsorption of molecules of the donor substrate and to the decrease of the reaction rate directed by the adsorption kinetics. In contrast to nickel oxide, where the decrease of the reduction rate with the increasing content of the ionic form of the super-stoichiometric oxygen has been observed, in the case of cupric oxide in the region of high doses no analogous correlation can be sought. The mechanism of the cupric oxide reduction proposed by Pavlyushenko¹⁰ includes both the adsorption-desorption process on the surface of the original oxide or on the interface and also the proper process of the reduction decomposition.

In samples irradiated by high doses of ionizing radiation the higher concentration of lattice defects and charge defects that form the active centers of the reduction decomposition will play the decisive role. The crystallochemical changes are accelerated as well as the nucleation. The higher concentration of defects of the interstitial-vacancy type and their local concentration gradients accelerate the transport of defects in the crystal by the Varley mechanism and thus also the decomposition process. The relatively high stability of defects formed by irradiation is confirmed by the fact that even after two months after the exposure the reduction rate of the irradiated samples was not the same as the reaction rate of the original oxides. A fast adsorption proceeds on these defects and the proper decomposition reaction will be the rate-determining process. These conclusions are in agreement with the higher rate of thermal decompositions of preirradiated salts of certain metals, ascribed to their highly defective structure²¹. In most cases a decrease of the activation energy of the reaction in comparison with the unirradiated sample has been observed²².

In the region of lower applied doses of γ radiation the increase of the value of the apparent activation energy of the reaction, observed also in oxides, the reduction rate of which remains practically unchanged (samples No 1 and 3 – Table III and Fig. 4), indicates the existence of a transition region of the rate-determining processes and of two antagonistic processes. With the increase of the applied dose the concentration of point- and charge defects will increase and the reaction will be accelerated. At the same time the equilibrium of the super-stoichiometric oxygen is shifted in favour of the strongly adsorbed ionic form that suppresses the donor adsorption of hydrogen molecules and decreases the reaction rate. In the sample No 4 (hydroxide origin, in the solution) with a highly developed surface and with a high concentration of active centers the first process will be the rate-determining step so that its reduction rate will increase with the applied dose. In the oxalate-origin oxide (sample No 6) the presence of the metallic phase will play a role. It will decrease its *p*-semiconducting properties and decrease the concentration of the majority of free charge carriers that will be further decreased by irradiation. The present metal will capture the free non-equilibrium holes that will recombine with electrons. The adsorption rate of the donor substrate will decrease with the increasing dose and even the reaction rate determined by adsorption will decrease. In samples No 1 and 3 these two processes will be in equilibrium in the region of lower applied doses so that the reduction kinetics will not be affected by the irradiation. At higher applied doses the first process will be the rate-determining step in all samples, leading thus to the acceleration of the reaction. The second process connected with the increase of the content of the ionic oxygen will further decrease the adsorption rate, which, however, will proceed with a higher rate than the subsequent reducing decomposition, limiting the overall reaction rate. No proportionality between the applied dose and the increase of the reaction rate can be expected due to the other

complicating factors accompanying the reduction of the studied samples of cupric oxide (exothermic reactions, presence of other components).

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