REDUCTION OF MIXED CuO–NiO OXIDES BY HYDROGEN AND THE EFFECT OF IONIZING RADIATION ON THE REDUCTION KINETICS

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Reduction of mixed CuO—NiO oxides by hydrogen was studied thermogravimetrically in the temperature interval $200-400°C$. Interaction of both components is the result of contact effects on the interface and is manifested by a pronounced dependence of the kinetics as well as of the activation energy of the reaction on the composition of samples. The rate of the over-all reduction attains its maximum value in the region of compositions where the ratio of both components is 1 : 1. Some samples, containing in their initial state basic carbonates which are used in preparing the oxides, undergo in the first phase a reductive decomposition. Preliminary heat treatment of the samples in an inert atmosphere at $500°C$ affects the dependence of the reduction kinetics on composition. Upon irradiation of oxides by γ-radiation (dose 10^7 J/kg) and by fast neutrons from an Am–Be source of the particle flow density $2 . 10^{16}$ neutrons/m^2 the concentration of the ionogenic form of superstoichiometric oxygen is modified and the rate of reduction of all samples increases. The mentioned effect which is accompanied by a decrease in the apparent activation energy of reduction is a function of composition and can be observed up to $400°C$. At higher temperatures of reduction or of previous heat treatment, the kinetic effects of irradiation disappear.

Nickel–copper alloys, often prepared by reduction of mixed oxides of both metals, are employed as catalysts of several chemical reactions, including some industrially important hydrogenation processes[1,2]. Whereas a number of studies were devoted to the mechanism and kinetics of reduction of nickel(II) oxide[3,4] or copper(II) oxide[5,6], only a little attention has hitherto been paid to the elucidation of these factors in the reduction of two-component mixed CuO—NiO oxides. Some authors[7] found a shortening of the induction period and an increase in the rate of reduction of pulverized NiO mechanically mixed with metallic copper in the ratio 2·8—50 w %. Addition of 5% of CuO had no effect on the reduction of NiO in dry hydrogen, however, it suppressed the inhibition effect of water vapour present in the reducing gas[8]. In a homogeneous solid solution of both oxides, containing 25% of CuO an increase in the reactivity of the system was proved when the reduction was carried out in the region of Néel temperature where the transition of the antiferromagnetic system into a paramagnetic takes place[9].

   Up to now, the data on the effect of ionizing radiation on the kinetics of reactions of the solid phase with gas are still rather incomplete. A decrease of the rate of reduction of NiO by hydrogen was observed[10] after irradiation by γ rays, if the applied dose exceeded the value $7 . 10^5$ J/kg and *vice versa*, an increase in the reduction rate was found after irradiation by protons[11] of the flow density 10^{20} protons/m^2. Changes in the reduction kinetics were also found in a two-com-

ponent NiO—ZnO system[12] with incorporated radiozinc 65 in dependence on specific activity of the samples.

This paper is aimed at the investigation of the reduction of the mixed CuO–NiO system of various compositions, however, in the case that no homogeneous solution is formed in the solid phase. At the same time the kinetics of reduction of these oxides was studied after irradiation by γ rays ^{60}Co and by fast neutrons of an Am–Be source.

EXPERIMENTAL

Mixed oxides of various compositions were prepared by calcinating basic carbonates, produced by precipitation of solutions of nickel(II) chloride and copper(II) nitrate with a solution of potassium carbonate, in 15% excess with respect to stoichiometry. Concentration of all solutions was 1 mol/l, all chemicals were of the reagent grade purity. The precipitates were left 48 h in their mother liquors. After filtration and thorough washing with redistilled water the preparations were dried on air for 24 h at 110°C and subsequently calcinated on air for 4 h at 400°C. After trituration in an agate mortar and sieving, the fraction of the grain size 0·05 — 0·20 mm was selected for further experiments.

The content of both metals in the samples was determined by electroanalysis. Specific surface areas were determined by adsorption of nitrogen at low temperatures. Fine structure of the samples was studied by X-ray diffraction according to Debye–Scherrer, or using the method of reverse beam. The content of superstoichiometric oxygen was determined iodometrically[13]. The samples were divided into several portions. The first of them was irradiated by γ rays from a ^{60}Co source by applying the dose of $5·4 . 10^6$ J/kg (further denoted as $D_{\gamma(1)}$), the second part was irradiated by a dose of $1·4 . 10^7$ J/kg (denoted as $D_{\gamma(2)}$) and the third one was irradiated by fast neutrons from an Am–Be source, of the flow density $2·06 . 10^{16}$ neutrons/m^2 (applied dose $D_n = 36·9$ J/kg). Reduction of mixed oxides was followed in the temperature interval 200—400°C under identical experimental conditions for both initial oxides and for the samples previously irradiated in the described manner. Denotation of samples, their composition as well as their specific surface areas are summarized in Table I.

The kinetics of reduction was studied by means of the apparatus, described in a previous communication[14]. The limiting conditions were found where the rate and kinetics of the reduction are independent, for a standard sample weight 50 g, of the flow rate of hydrogen for any arbitrary composition of the sample. Accordingly, the flow rate of hydrogen 56 ml/min was employed in our experimental arrangement.

RESULTS

Conditions of preparation of mixed oxides, (particularly time and temperature of calcination) lead to the formation of a multicomponent system (Table I) involving in addition to oxides also elementary copper (samples No 4 and 12) or also undecomposed basic carbonates. The metallic phase was also identified by microstructural analysis. The presence of carbonates in samples with low total content of both oxides was proved by reaction with $Ba(OH)_2$. With the exception of samples 4 and 12 only selective reflexions were found over the whole range of compositions, corres-

ponding to copper(II) and nickel(II) oxides. Under the given experimental conditions, precipitation of initial solutions with alkali carbonate leads to the formation of basic carbonates with undeveloped structure or of amorphous character, which persists up to the temperature of decomposition so that they cannot be proved by means of X-ray diffraction[15]. Using the reversed beam method it was found that the value of the parameter of cubic lattice of NiO is not affected by increasing content of CuO. The absence of solid solution of both oxides is in agreement with the results obtained under entirely different conditions of preparation[9] leading to a solid solution CuO--NiO. For the sake of comparison the study was performed of the reduction of samples containing undecomposed carbonates as well as of those subjected to additional heat treatment under the conditions described further leading to the decomposition of further portions of carbonates.

The studied system is characterized by the non-additivity of specific surface areas of both pure components with respect to their percentual content in the mixed oxide (Table I). Investigation of the samples by means of electron scanning microscope in the magnification region $5 \cdot 10^2$ to 10^4 has demonstrated a relatively low degree of aggregation of elementary crystallites and a varying degree of dispersity and surface sintering in dependence on composition. Also the measured values of specific surface areas for samples of different composition agree with the above mentioned results. Surface area and crystalline structure are not affected by the applied ionizing radiation in the range of doses used in our experiments.

TABLE I

Denotation, Composition and Specific Surface Areas S of Mixed CuO–NiO Oxides

Samples	Weight %					S m^2/g
	Cu	Ni	CuO	NiO	CuO + NiO	
1	0·33	69·40	0·42	88·15	88·57	39·80
2	0·66	50·30	0·83	63·90	64·73	7·22
3	3·70	59·76	4·63	75·90	80·53	11·32
4	13·90	70·40	17·38	89·55	106·93	53·10
5	24·80	52·10	31·05	66·30	97·35	54·60
6	32·20	43·50	40·30	55·35	95·65	32·80
7	33·80	28·30	42·30	35·95	78·25	1·96
8	38·90	36·20	48·65	46·00	94·65	2·65
9	40·10	12·53	50·08	15·91	65·99	1·59
10	50·10	0·13	62·80	0·17	62·97	2·45
11	68·50	7·70	85·80	9·80	95·60	8·02
12	84·10	—	105·00	—	105·00	17·40

The content of the ionogenic form of superstoichiometric oxygen changes distinctly in dependence on the composition of sample. No simple relation, however, was found between these two quantities. Irradiation by γ rays and fast neutrons leads to an increase in the concentration of the ionogenic oxygen, irrespective of the composition of the sample (Table II). Concentration of oxygen increases with increasing dose applied.

Reduction rates and lengths of the induction period at constant temperature are markedly dependent on the composition of samples (Figs 1 and 2, curves *1*). The plots represent the time courses of reduction of samples 1 and 10 from Table I at 320°C. With increasing reduction temperature the delay (sample 10) becomes shorter and at 400°C the curve has a practically smooth course.

Theoretical weight losses of samples, calculated for a given weight portion and composition, assuming a total reduction of both oxides (CuO, NiO) present in the system, are compared in Table III with maximum experimental losses attained at 350°C.

TABLE II

Weight % of Superstoichiometric Oxygen of Some Samples of the CuO–NiO Series and the Same Samples Irradiated by γ Rays and Fast Neutrons

Samples	Non-irradiated	Irradiated by γ rays		Irradiated by neutrons
		$D\gamma_{(1)}$	$D\gamma_{(2)}$	
1	0·067	0·093	0·101	0·117
2	0·036	0·060	0·084	0·116
3	0·057	0·085	0·091	0·127
7	0·011	0·050	0·081	0·046
8	0·007	0·008	0·047	0·055
9	0·000	0·000	0·052	0·049
10	0·000	0·005	0·022	0·054
12	0·015	0·023	0·122	0·064

TABLE III

Theoretical and Experimental Weight Losses of Samples at Reduction Temperature 350°C

Sample	1	2	3	4	5	6	7	8	9	10	11	12
Loss (mg) theor.	9·30	6·79	8·50	11·14	10·11	9·84	8·01	9·70	6·68	6·30	9·61	10·00
Loss (mg) exp.	10·40	10·00	12·90	10·20	10·10	10·30	13·10	12·00	12·40	14·40	9·45	9·50

It is evident that with samples containing an undecomposed salt the degree of reduction exceeds the theoretical value. However, the reduction curves did not, in àll cases, exhibit such marked delays as it was in the case of sample 10 where the degree of reduction higher than theoretical attains its maximum. Samples in which the sum of both components approaches 100% (Table I) show a very good agreement of theoretical and experimental values. A lower degree of reduction than theoretical was found in samples which according to analysis contain free copper (samples 4 and 12).

The high degree of interaction of both oxides in the system is indicated by the finding that at 200°C only copper(II) oxide is reduced in a measurable rate in a homo-
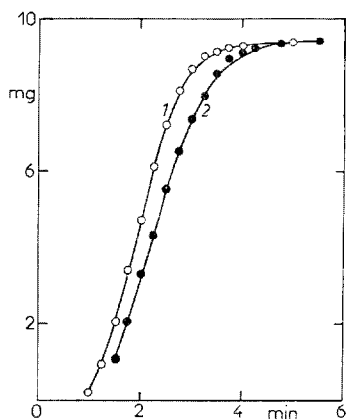

FIG. 1

Time Courses of the Reduction of Sample 1 at 320°C

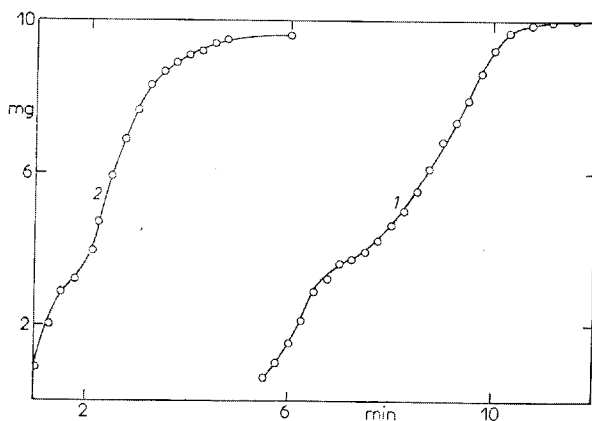*1* Non-irradiated sample, *2* sample irradiated by γ rays $D_{\gamma(1)}$.

FIG. 2

Time Courses of the Reduction of Sample 10 at 320°C

1 Non-irradiated sample, *2* sample irradiated by γ rays $D_{\gamma(1)}$.

geneous mechanical mixture prepared from pure CuO (sample 12) and NiO of analogous origin in the ratio 1 : 1. However, a total reduction of both components takes place at the same temperature in a mixed sample of any arbitrary composition, *i.e.* also in the presence of a very small amount of CuO (sample 1).

The effect of composition on the reduction rate is evident from Fig. 3 (curve 2) illustrating the dependence of maximum reduction rate, related to unit surface area of the sample (specific V_{max}), on composition. Mixed oxides are reduced at the highest rate in the region where the ratio of both components is 1 : 1.

Previous irradiation of samples by γ rays affects the dependence of the reduction kinetics on composition in a characteristic manner. Curves *2* in Figs 1 and 2 represent the time courses of reduction of irradiated $(D_{\gamma(1)})$ samples 1 and 10. Comparison with the reduction courses of initial samples (curves *1*) shows that with sample 1 (excess of NiO) the length of the induction period remains practically unaffected and the oxide is reduced more slowly. Contrary to this, reduction of irradiated sample 10 (excess of CuO) proceeds at a higher rate and the induction period is considerably shortened. Irradiation by γ rays of a higher dose $(D_{\gamma(2)})$ results unambiguously in an increase of the reduction rate (Fig. 3, curve *1*). In the region of high excesses of NiO, however, the increase of the reduction rate is not so marked as in samples with higher contents of CuO. The mentioned effects can be still observed at reduction temperature 380°C. The difference between the kinetics of reduction of samples of the basic series and the irradiated ones, obtained at still higher temperatures, lie already in the limits of experimental errors. It follows from the comparison of maximum reduction rates of some samples of the series with those of samples irradiated by fast neutrons and reduced under identical conditions (reduction temperature 290°C) (Table IV) that irradiation by neutrons of the flow density of $2 \cdot 06 \cdot 10^{16}$ neutrons/m^2 leads, too, to a detectable increase in the reduction rate. The lowest effect is found with sample 12 (pure CuO).
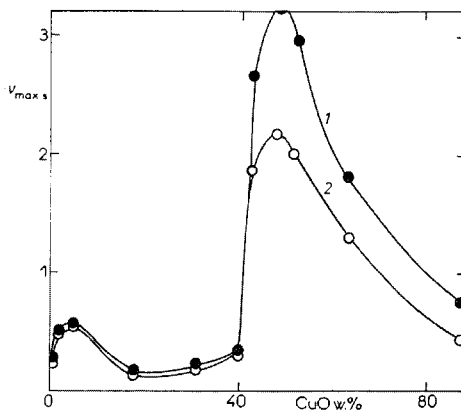

Fig. 3

Dependence of Specific Maximum Reduction Rate (mg/min m^2) of Samples of the CuO–NiO Series on Composition at 320°C

1 Samples irradiated by γ rays $D_{\gamma(2)}$, *2* non-irradiated samples.

TABLE IV

Maximum Reduction Rates (mg/min) of Some Non-Irradiated Samples of the CuO–NiO Series and of the Same Samples Irradiated by Fast Neutrons of the Particle Flow Density $2 \cdot 06 \, . \, 10^{16}$ n/m^2

	Sample	1	2	3	7	8	9	10	12
V_{max} {	non-irradiated	1·6	0·8	1·6	1·6	4·0	0·8	1·6	9·2
	irradiated by n	2·8	2·8	4·0	5·6	8·0	2·0	3·2	9·6

Samples selected both from the basic series and from the irradiated oxides were oxidized, after primary reduction, in a stream of air up to constant weight. Inlet of hydrogen started the secondary reduction. All three mentioned processes took place at constant temperature 320°C. In general, the degree of oxidation increases with increasing content of CuO. Since all oxide formed in this process is totally reduced in the subsequent secondary reduction, also the degree of this reduction increases with increasing content of CuO. However, it does not attain the original value of the primary process or the value for pure CuO. The effect of preliminary irradiation is completely eliminated by primary reduction. Up to c. 50% CuO secondary reduction proceeds at a lower rate than the primary process, at higher CuO contents the rate of secondary reduction is higher than that of primary reduction.

Effect of heat treatment of samples in an inert atmosphere on the reduction kinetics was investigated at the temperatures of heat treatment 350 and 500°C. Prior to reduction the samples were treated for 60 min in a stream of dry nitrogen which was freed of traces of oxygen. Treatment in the region of commonly used reduction temperatures of the series, *i.e.* up to 350°C, is without any effect on the kinetics of reduction of non-irradiated samples. Higher rate of reduction of samples irradiated by γ rays $\left(D_{\gamma(2)}\right)$ and neutrons remains practically unchanged. Treatment at 500°C brings about a weight loss of the samples. The delay on the curve of subsequent reduction is shorter, but even under the mentioned conditions the decomposition of the relatively stable phase of the present basic carbonates is not complete. According to analysis, the samples treated in this way contain 92% oxides on the average, with respect to stoichiometry. In addition, at this temperature kinetic effects caused by irradiation are eliminated and courses of the reduction of irradiated and thermally treated samples are identical with those found in the reduction of initial oxides. Treatment at 500°C results in a higher reactivity of samples, manifested by their higher reduction rate. Activation depends on the composition of mixed oxides and becomes effective in samples containing excess NiO. In the second region of compositions

of this series (excess CuO) the reduction rate of thermally treated samples is lower as compared with initial oxides (Fig. 4), the reduction temperature being in all cases 320°C.

In order to describe quantitatively the kinetics of reduction of samples of the series CuO–NiO, we applied the equation of Prout-Tompkinson, modified by Bond[6], which reflects in most cases the reduction kinetics of CuO, and the equation of zonal model of decomposition of solid substances[16], valid for the kinetics of reduction of NiO or of mixed systems on the basis of NiO. For the oxides studied in our case the first equation can only be applied to the reduction of samples with predominating content of CuO ($>80\%$) whereas the second equation is valid for oxides with high content of NiO. When applied in this way, the equations hold in a relatively wide interval of the reduction degree $\alpha = 0.05 - 0.9$. The whole range of composition is best fitted by the equation of Avrami[17] and Erofeev[18] ($-\log (1 - \alpha)^{1/n} = k \cdot t$, with the exponent $n = 2$. In this equation α is the degree of reduction in time t and k is a constant. Fig. 5, where this equation is applied to reduction of sample 8 (ratio of both components 1 : 1) shows the linearity in the region of higher reduction temperatures and for lower temperatures up to $\alpha \approx 0.6$. The apparent activation energy of reduction was calculated from the temperature dependences of the rate constants of the above equation. In non-irradiated samples the value of activation energy decreases with increasing content of CuO in the interval $11.5 \cdot 10^4 - 5.5 \cdot 10^4$ J/mol.
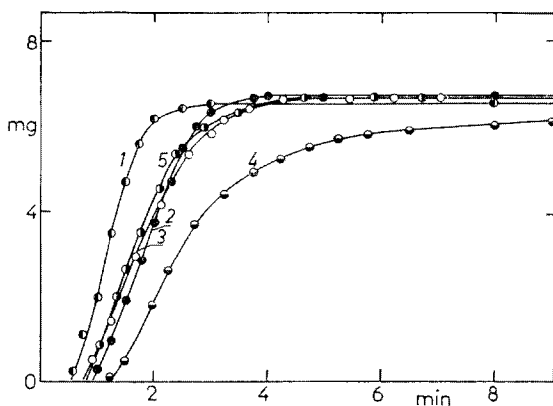

FIG. 4

Time Courses of the Reduction of Sample 2 at 320°C, Irradiated and Thermally Treated in Different Ways

Samples: *1* irradiated by neutrons and treated at 350°C, *2* irradiated by neutrons and treated at 500°C, *3* irradiated by γ rays $D_{\gamma(2)}$ and treated at 500°C, *4* original and non-treated sample, *5* original, non-iraadiated and treated at 500°C.

Irradiation by neutrons and γ rays $(D_{\gamma(2)})$ leads to a decrease in the activation energy which attains the values between $9.7 \cdot 10^4 - 4.9 \cdot 10^4$ J/mol in dependence on composition.

DISCUSSION

From the experimental data it is evident that in a two-component CuO–NiO system total reduction of both components takes place over the whole range of compositions, under the conditions used. The presence of copper(II) oxide promotes the reduction of nickel oxide provided both components are present in the mixed oxide. In a homogeneous mechanical mixture both components behave practically independently of each other and at 200°C the reduction rate of NiO is no more measurable. Similar behaviour was experimentally demonstrated in the study of the reduction of an analogous system, however, prepared by thermal decomposition of mixed crystallic nitrates[19]. Consequently, the difference in the genesis of oxides has no essential effect, as far as reduction is concerned, on the character of interaction of both components. The reducibility of both pure oxides is given by their thermodynamic properties. According to the results of microstructural analysis, the system does not form a homogeneous solution in the solid phase. Thus it can be assumed that the interaction of both components is realized through contact effects on their interface. As to the genesis and conditions of preparation, the system of nitrate origin apparently consists only of oxides of both metals, which have an average value of the sum of weight percent of $97 - 99\%$, as related to the stoichiometry of CuO and NiO, over the whole concentration range[19]. Some of the studied samples of carbonate origin showed the presence of elementary copper or of relatively stable non-decomposed basic carbonates. Even after additional thermal treatment at 500°C for 1 h their total decompo-
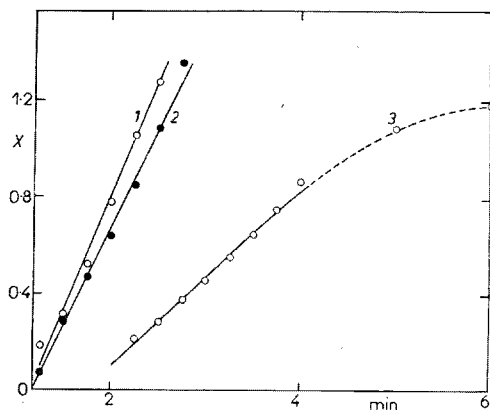

FIG. 5

Application of the Equation of Avrami[17] and Erofeev[18] to the Kinetics of Reduction of Sample 8 at Different Temperatures $X = [-\log(1 - \alpha)]^{1/2}$
1 380°C, *2* 350°C, *3* 290°C.

sition is not attained. The stability of carbonates is probably caused by the presence of oxides in the system. The amount of non-decomposed carbonates is variable, depending strongly on the composition of samples. Composition of basic carbonates formed in preparing the samples by precipitation of the solution of initial salts by alkaline carbonate changes. The decomposition temperatures of basic carbonates are different in a certain interval, and consequently also the degree of decomposition and thus also the content of carbonates varies in dependence on composition at constant temperature of calcination of samples in the whole series. Experimental results indicate that calcination temperatures higher than 500°C lead to total decomposition of carbonates to the oxides, but, at the same time they cause also the thermal decomposition of CuO under the formation of Cu_2O, or even elemental copper[20]. Principal curves of the time course of reduction of samples containing carbonates (Fig. 2) can be interpreted[19] so that the first stage is a reductive decomposition of carbonates, a reaction, preceding the subsequent reduction of the formed oxides. However, the over-all kinetic behaviour of the system is complicated. The relatively high value of apparent activation energy of the reductive decomposition, $15 \cdot 1$. $. 10^4$ J/mol, allows us to expect that in addition to the consecutive processes also a parallel reduction of mixed oxides proceeds which are already present in the initial system. These oxides affect the kinetics of the reductive decomposition of carbonates. With increasing temperature the delay on the time course of reduction becomes shorter and at 400°C the two processes cannot be distinguished any more. Analogous conclusions can be found in paper[19].

The range of values of the activation energy in dependence on composition, as well as further experimental results indicate that in the region of excess of either of the components the effect of the same component becomes effective. With regard to the fact that the kinetics of reduction of the studied system can be described also by the equation of Avrami[17] and Erofeev[18] over the whole composition range only with a limited validity, the values of specific maximum reaction rates (Fig. 3) were used to estimate the effect of composition and of further factors on the kinetics of the studied reaction. As follows from the experimental results, already a small amount of CuO promotes the reduction of nickel(II) oxide at temperatures at which it would not be reduced alone under the given conditions. It is evident that at all temperatures the highest reaction rate is attained when the ratio of components is 1 : 1. This finding is in perfect agreement with the results of study of the reduction of mixed CuO–NiO crystals of nitrate origin[19]. In these experiments the system did not contain carbonates. The nature of the dependence of the reaction rate on composition allows the assumption that the reduction takes place on elementary contact sites of both oxides, its rate being proportional to total concentration of these contacts and thus also to the total interface area. It is probably due to the effect of reduced metallic copper which takes away oxygen from nickel(II) oxide. The removed oxygen is then reduced by hydrogen according to thermodynamic properties of CuO. In the course of the

reaction the active interface is represented by the system NiO–Cu, or NiO–Cu_2O. In the region of excess nickel(II) oxide, the concentration of elementary reaction zones is proportional to the concentration of CuO and increases with its increasing content up to equal percentual content of both components. In samples with excess CuO the concentration of interface analogously increases with increasing content of NiO, since the reaction zone is formed by contacts of both components. Consequently, their interaction attains maximum at their ratio 1 : 1; concentration of elementary contacts, their total area and accordingly also the reduction rate attain their maximum values. The effect of mutual interaction of contacts increases with increasing reaction temperature which is also manifested in the shape of the dependence of the reaction rate on composition. The symmetry of the curve is improved and the reduction rate increases continuously up to a maximum, in accordance with the presumed model.

The results of reoxidation experiments show that the primary reduction results in a microheterogeneous system of both reduced metals. With respect to experimental conditions, especially to the extremely short time of primary reduction and the immediately started subsequent oxidation there are no optimum conditions for the formation of a homogeneous alloy[2]. Thus, the effect of the major component predominates in the region of excess of either of the components, however, also their interaction becomes effective. In accordance with previous results of the study of two-component systems based[21] on NiO, the degree of its oxidation increases with the content of the second component. Analogously, the degree of secondary reduction increases with increasing content of CuO, since both primary oxides are completely reduced in the secondary process. Interaction of both oxides which are formed in oxidation process is of course weaker than that in the initial system. Activity of the contact interface and consequently also the effect of CuO are also lower so that the secondary reduction of samples with excess NiO proceeds at a lower rate than the primary reduction of mixed oxides, whereas the rate of secondary reduction increases with increasing content of CuO.

From the experiments also the positive effect follows of heat treatment of samples in an inert atmosphere at 500°C, *i.e.* an increase of the reduction rate of samples containing excess NiO. A similar effect was observed also with the two component system[21] NiO–ZnO and consequently it is probably connected with the presence of NiO in the system. Increase in the reduction rate of heat treated samples is probably due to uncovering of new centers through desorption of trace amounts of water which is present in systems with superstoichiometric nickel(II) oxide[21]. Further it can be assumed that in the case of mixed oxides CuO–NiO thermal treatment enhances the contact of both components on their active interface, as a result of increased diffusion mass transfer at higher temperatures. This kind of activation of samples, however, cannot be decisive, since the reduction rate of heat treated oxides would have to increase proportionally to the concentration of elementary contacts. The highest

reduction rate should be found with the treated samples having equal percentage of both components. This, however, was not found.

Kinetics of reduction of mixed CuO–NiO oxides is further considerably affected by irradiation by γ rays and by fast neutrons and that also in dependence on composition. Figs 1 and 2 show that irradiation by γ rays applied in lower dose $\left(D_{\gamma(1)}\right)$ leads to a decrease in the reduction rate of samples with excess NiO and *vice versa*, to an increase in the reduction rate of samples with excess CuO. At the same time, the induction period is practically unchanged in the former case and in the latter case it is shortened. Application of a dose, higher by an order of magnitude $\sim 1\cdot 4$ . . 10^7 J/kg and irradiation by neutrons lead to an acceleration of the reaction over the whole range of compositions. However, it is evident from Fig. 3 that the positive effect is quantitatively different in various regions of composition, wherein the overall character of the dependence of the reaction rate on composition is the same as with non-irradiated samples. The relative change of maximum specific reduction rate (expressed in per cent) of irradiated samples compared with initial oxides can be quantitatively expressed by quantity $\varDelta$ in terms of the relation $\varDelta = 100 . (V^+ - V)/V$, where V^+ pertains to irradiated and V to non-irradiated samples, respectively. Table V, where the values of $\varDelta$ are presented for individual samples of the series, shows that the effect in general is lower with samples containing excess NiO.

Increase of the reaction rate caused by previous irradiation may be assumed to be primarily conditioned by the formation of new centers, lattice defects and defect of the charge character which can be stabilized on the interface, thus increasing its activity. At the same time further positive factors become effective, which accelerate the decomposition process. It is known[22] that with increasing concentration of point defects in the structure the reduction rate increases as a result of increased crystallochemical change and formation of nuclei. Thermal decompositions of previously irradiated salts of some metals proceed at a higher rate than those of the same non--irradiated samples, evidently also due to the strongly defective structure[23]. Higher concentration of defects of the interstitial-vacancy type and their local concentration gradients accelerate the transport of defects in the crystal *via* the Varley mechanism and consequently also the decomposition process is accelerated[11]. These assumptions

TABLE V

Dependence of the Quantity $\varDelta$ (%) on the Composition of Samples at Reduction Temperature 320°C

Sample	1	2	3	4	5	6	7	8	9	10	11
$\varDelta$	8·4	10·3	11·5	16·5	18·2	19·4	45·1	50·0	50·0	39·6	80·0

are supported by the following experimental results: reduction of irradiated samples proceeds with a lower activation energy and the activation energy of reductive decomposition of carbonates of irradiated samples attains a value which is practically half $\left(E_a = 7{\cdot}7 \,.\, 10^4 \,\text{J/mol}\right)$ of that of decomposition of an non-irradiated sample. In the region of higher reduction temperatures (about 400°C) the differences in the kinetics of initial and irradiated oxides are no more detectable. Kinetic effects caused by irradiation are also completely eliminated by heat treatment at 500°C. At higher temperatures the concentration of nonequilibrium defects in the system decreases owing to regeneration processes and the quantity Δ converges to zero. However, in the case of samples with excess of nickel(II) oxide participation and effect of adsorption processes is manifested. In papers[10,12] a correlation is reported between the content of the ionogenic form of superstoichiometric oxygen in NiO and its reduction rate. Upon irradiation the equilibrium between various forms of superstoichiometric oxygen is shifted in favour of the ionogenic form, *via* a mechanism given in paper[12]. This process occurs also in the system CuO–NiO (Table II). Provided that the surface adsorption process is the rate determining step, the reduction rate of NiO must decrease, according to the concepts of electron theory, with increasing content of the ionogenic form of oxygen, which was also verified in papers[10,12]. From Fig. 1 it is evident that irradiated samples containing excess NiO are reduced at a lower rate than initial oxides. Also the highest reduction rate of an irradiated sample with excess CuO, as compared with non-irradiated oxide, (Fig. 2) is in agreement with the finding[24] that no similar correlation between the content of superstoichiometric oxygen and the reduction kinetics can be found in the case of copper(II) oxide. Application of higher doses of irradiation leads to an increase in concentration or activity of centers with all samples of the series, regardless of their composition. At the same time also the concentration of ionogenic form of superstoichiometric oxygen increases. As a result of this, the rate of reduction of nickel(II) oxide and of those samples in which nickel(II) oxide represent the major component, decreases. Evidently, in these oxides the accelerating processes are compensated by a competitive process, causing a slow-down of the reduction. With respect to the mentioned effect the values of Δ will be lower in the region of excess of NiO than in the second half of the series, which is in full agreement with our results (Table V).

REFERENCES

1. Hall W. L., Emmett P. H.: J. Phys. Chem. *62*, 816 (1958).
2. Ljubarskij G. D., Jevzerikhin E. I., Slinkin A. A.: Kinet. Katal. *5*, 311 (1964).
3. Chufarov G. I., Zhuravleva M. G., Tatevskaya E. P.: Dokl. Akad. Nauk SSSR *73*, 1206 (1950).
4. Frety R., Tournayan L., Charcosset H.: Ann. Chim. (Paris) *9*, 341 (1974).
5. Kurchatov M. S., Lambijev D.: Dokl. Bulg. Akad. Nauk *17*, 629 (1964).
6. Bond W.: J. Phys. Chem. *66*, 1573 (1962).

7. Verhoewen W., Delmon B.: C. R. Acad. Sci., Ser. C *262*, 33 (1966).
8. Charcosset H., Frety R., Grange P., Trambouze Y.: C. R. Acad. Sci. *267*, 1746 (1968).
9. Grange P., Charcosset H., Gallerot P., Turlier P., Vialle J.: J. Solid State Chem. *11*, 26 (1974).
10. Yamashina T., Nagamatsuya T.: Bull. Chem. Soc. Jap. *38*, 507 (1965).
11. Simnad M., Smoluchowski R., Spilners A.: J. Appl. Phys. *29*, 1630 (1958).
12. Pospíšil M., Cabicar J.: This Journal *39*, 3056 (1974).
13. Weller S. V., Volts S. E.: J. Amer. Chem. Soc. *76*, 4695 (1954).
14. Pospíšil M., Cabicar J., Rejholec V.: This Journal *35*, 1319 (1970).
15. Dreyer H., Mehring D.: Z. Anorg. Allg. Chem. *300*, 113 (1959).
16. Roginskij S. Z., Schulz E.: Z. Phys. Chem. A *138*, 21 (1928).
17. Avrami M.: J. Chem. Phys. *9*, 177 (1941).
18. Erofeev B. V.: Dokl. Akad. Nauk SSSR *52*, 511 (1946).
19. Cabicar J.: *Thesis.* Czech Technical University, Prague 1964.
20. Schmahl N. G.: Angew. Chem. *65*, 447 (1953).
21. Pospíšil M., Cabicar J.: This Journal *38*, 2016 (1973).
22. Vlasov V. G., Zhukovskii V. M.: Kinet. Katal. *4*, 76 (1963).
23. Mohanty J. R., Ray M. N.: Indian J. Chem. *3*, 37 (1965).
24. Pospíšil M.: Unpublished results.

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