REDUCTION OF MIXED NiO–U_3O_8 OXIDES BY HYDROGEN AND THE EFFECT OF GAMMA RADIATION ON THE PROCESS

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Received October 22nd, 1980

The reduction of mixed NiO–U_3O_8 oxides of various composition by hydrogen was studied in the temperature range 350—590°C using the thermogravimetric method. An addition of nickel oxide in the amount of few per cent increases the reduction rate of U_3O_8 and substantially decreases the initial temperature of its reduction. The reduction of pure U_3O_8 proceeds with a maximum and steeply decreasing rate in the region of the oxide composition $U_3O_8 \rightarrow UO_{2.59}$ and with a constant rate in the region $UO_{2.59} \rightarrow UO_{2.25}$. In the heterogeneous two-component system the reduction rate increases with the increasing content of nickel oxide. The reduction of the stoichiometric NiO is retarded by a small homophaseous addition of U_3O_8. Radiation oxidation of U^{4+} ions proceeds during the pre-irradiation of the samples with gamma radiation at a dose of 1 MGy and the reduction rate of samples with a surplus of U_3O_8 is decreased. With the increasing content of nickel oxide the negative effect of radiation is continuously changed into a positive effect (an increase of the reduction rate). The reduction kinetics of irradiated samples is in both homogeneous extreme regions of composition governed by the adsorption processes and in the heterogeneous region it depends on the radiation-induced defects with strongly temperature-dependent stability.

The thermal reduction of uranium dioxide, the physicochemical properties of which depend substantially on the method of its preparation, is the basic process in the production of non-pyroforic uranium powder. From this point of view a considerable interest has already been devoted to the studies of the reduction of uranium oxides of various stoichiometry[1,2] by gases and in lesser extent also to the reduction of these oxides with an incorporated homogeneous[3] or heterogeneous[4] admixture in a limited range of composition. Recently also the reduction of higher oxides of uranium and of oxides of polyvalent metals is studied with respect to their catalytic properties[5] which can be modified by the presence of the other component that also changes the kinetics and reduction degree of the original oxide.

From this standpoint the reduction of mixed NiO–U_3O_8 oxides of various composition by hydrogen has been studied in this work together with some physicochemical properties of this system. The reactivity of mixed oxides has been also modified by pre-irradiation with ^{60}Co gamma rays and the effect of irradiation of the reduction kinetics has been followed.

EXPERIMENTAL

Mixed oxides of various composition were prepared by the thermal decomposition of mixed nitrates. The solutions of $Ni(NO_3)_2.6\,H_2O$ and $UO_2(NO_3)_2.6\,H_2O$ of the chemical purity grade (concentrations 1 mol dm^{-3}) were filtered and mixed in the required ratios. After evaporation to dryness on a water bath the crystalline product was heated on air in an electric resistance oven for 4 h at the temperature of 800°C and pulverized in an agate mortar. The sample was dissolved in concentrated nitric acid and after the precipitation of ammonium diuranate the content of nickel was determined in the filtrate using the complexometric titration. The content of uranium was determined indirectly in an aliquot of the solution, without masking or separation of nickel, using the titration with ammonium vanadate[6]. The microstructure of mixed oxides was studied using the Debye–Scherrer and the back-reflection methods. The size of the coherent regions of both oxides was calculated from the half-width of the diffraction lines. The specific surface area was determined by the nitrogen adsorption at low temperatures and the morphology of mixed oxides and reduced samples was studied using the electron scanning microscope Jeol JSM-50A. A part of samples was irradiated with ^{60}Co gamma rays at a dose of 1 MGy. The content of ionogenic superstoichiometric oxygen or the oxidation ability of the surface of the original mixed oxides and of the irradiated samples was determined by iodometry. The reduction was followed in the temperature region from 350 to 590°C under identical experimental conditions both for the original oxides and for the pre-irradiated samples. The reduction kinetics was studied by the thermogravimetry[7] under the conditions under which the time dependence and the reduction rate are independent of the hydrogen flow rate (the standard sample weight of arbitrary composition was 50 mg, in the case of two samples with a high excess of U_3O_8 100 mg, and the hydrogen flow rate was 56 ml/min). The notation of mixed oxides, their composition, specific surface areas and the size of the coherent regions are summarized in Table I.

RESULTS AND DISCUSSION

According to the results of the analysis (Table I) the original salts decompose – under the given conditions – forming two-component mixed NiO–U_3O_8 oxides. X-ray diffraction revealed also the presence of cubic nickel oxide and of the orthorhombic phase of α-U_3O_8 in the system. The samples No 3 to 5 (Table I) gave other selective reflections which probably belong – due to the optimum ratio of both components – to a special phase NiO.3 UO_3 or, respectively, NiU_3O_{10} that was described in the paper[8]. In these samples the maximum reduction degree, higher than the theoretical value calculated under the assumption of the total reduction of NiO to Ni and U_3O_8 to UO_2 has been found. Because the upper limit of the thermal stability of this compound is about 980°C, the samples were thermally treated for 4 h on air at the temperature of 1 000°C. Disappearance of the characteristic reflections of the new phase indicates its thermal decomposition during the treatment. At the same time the reduction degree of the product, the stoichiometry of which corresponds to the other samples of the series, decreased.

The mutual interaction of both components is demonstrated also by the non-monotonous dependence of the specific surface area on the composition which has a maximum at about 10–30 wt. per cent of U_3O_8 in the sample (Table I). Relatively low values of the surface of both pure oxides and mixed oxide samples ($<10\,m^2/g$) are given by their origin and they are characteristic for oxides obtained by the thermal decomposition of nitrates[9]. Due to the high temperature of the thermal decomposition of the original salts also sintering processes participate on the decrease of the surface. In the region of nickel oxide excess the increase of the specific surface area of samples may be connected with the increasing content of U_3O_8 and with the conspicuous decrease of the crystallite size of the major component (NiO) up to about 30 wt. per cent of U_3O_8. On the other end of the sample series an addition of a small amount of NiO decreases the size of coherent regions of the major component (U_3O_8 in this case) by an order of magnitude – *cf.* Table I. In these samples, however, the surface area is not given by the size of elementary crystallites. In the whole range of composition a very good correlation between the specific surface area and the calculated grain size of individual samples has been observed (Fig. 1). Assuming that all particles have a uniform shape of small cubes (Fig. 2)* the average size of particles can be expressed by the relation $a = 6/\varrho\,.\,S$, where a is the edge length (μm), ϱ is the sample density (g/cm^3), and S is the specific surface area (m^2/g). From

TABLE I

Sample assignment, their composition, specific surface area, and the size of coherent regions (L) in mixed NiO–U_3O_8 oxides

Sample	Wt.%			S m^2/g	L, nm	
	NiO	U_3O_8	NiO + U_3O_8		NiO	U_3O_8
1	—	98·99	98·99	1·9	—	265·2
2	1·63	97·46	99·09	1·3	—	75·4
3	8·48	90·74	99·22	1·9	—	47·0
4	13·30	85·98	99·28	1·8	—	—
5	19·58	80·39	99·97	2·3	68·0	—
6	28·81	71·17	99·98	4·2	78·9	—
7	37·94	60·55	98·49	5·1	32·6	—
8	49·60	50·34	99·94	5·6	69·9	47·1
9	56·17	41·79	97·96	6·2	45·8	95·1
10	68·35	30·95	99·30	9·9	44·5	84·8
11	78·27	20·96	99·23	9·2	71·9	63·8
12	84·01	15·60	99·61	9·0	61·6	67·0
13	86·64	10·77	97·41	9·4	72·3	69·0
14	97·25	2·11	99·36	5·2	96·0	—
15	99·69	—	99·69	1·6	174·1	

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* See insert opposite p. 3200.

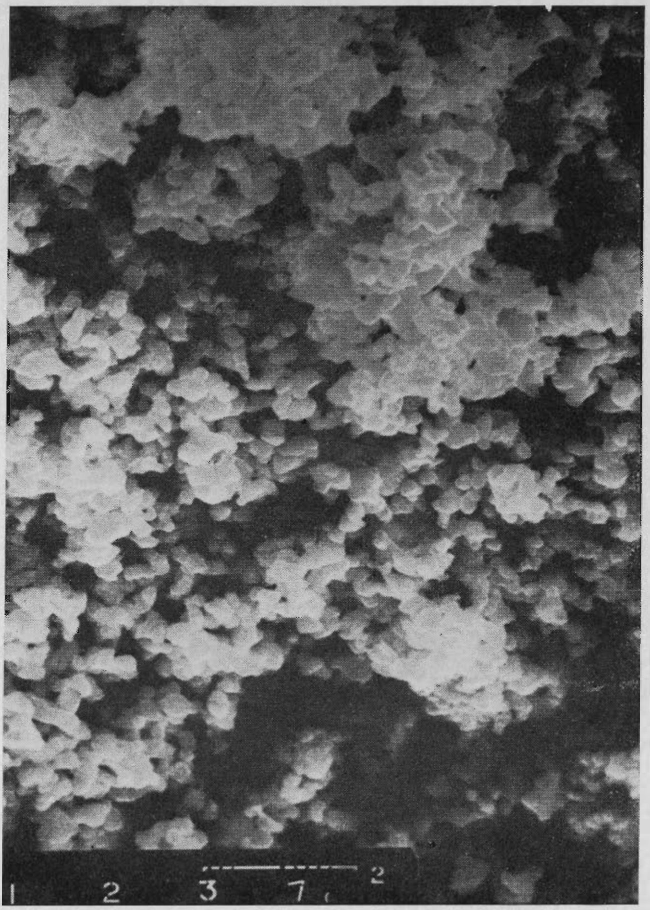

FIG. 2

Morphology of the sample No 1 (Table I). A micrograph taken by the electron scanning microscope, magnification 10^4 (the distance indicated above the number corresponds to 2 μm) the mentioned correlation and from the morphology of samples it is evident that in the mixed oxides under study the surface area is given by the geometric surface of grains and not by the surface of pores which is in agreement with the generally low values of this quantity in the whole series of samples.

Table II summarizes the results of the iodometric determination of the content of the superstoichiometric oxygen or of the surface oxidation ability, respectively, and of the same quantity normalized to the unit surface area of the sample. In the case of nickel oxide this quantity represents the surface concentration of Ni^{3+} ions that are in equilibrium with the ionogenic forms of superstoichiometric oxygen. In the case of U_3O_8 the n-type semiconductor character, which is connected with the excess of the electropositive metallic component of the oxide, has been experimentally proved in agreement with the published data[2]. The given quantity gives then the surface concentration of U^{6+} ions. From Table II it follows that in the both extreme regions of the series the low per cent addition of the other component decreases this quantity and the gamma irradiation increases it even by an order of magnitude in samples with high excess of U_3O_8. The charge interaction of both components can be interpreted in terms of the theory of semiconductors. Incorporation of U^{4+}, or U^{6+} ions, respectively, into the NiO lattice decreases the concentration of Ni^{3+} ions and the corresponding part of the superstoichiometric ionogenic oxygen. In the region of U_3O_8 excess the addition of nickel oxide decreases the concentration of U^{4+} ions that are oxidized to higher valence states due to the condition of the lattice electroneutrality. The substitution of U^{4+} ion by Ni^{2+} means that two U^{4+} ions are transformed into U^{5+} so that two positive holes are formed. Another possibility of the charge compensation is given by the formation of vacancies in the oxygen sublattice of the uranium oxides. However, from the point of view of the discussed depen-

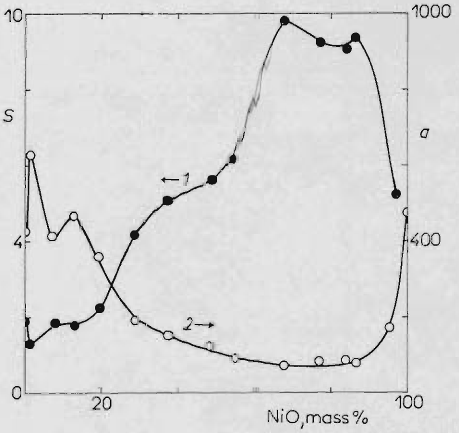

FIG. 1

Specific surface area S (m^2/g) and the grain size a (nm) as a function of the composition 1 S, 2 a

dence the decrease of the surface oxidation ability in this region is caused by another process, *i.e.*, by the reduction of the determined U^{6+} ions by Ni^{2+} ions which decreases their concentration.

The content of the ionogenic form of the superstoichiometric oxygen is by one or two orders of magnitude lower than in most two-component oxide systems on the basis of nickel oxide[10,11]. This fact is evidently connected with the high stoichiometry of nickel oxide which has the typical yellow-green colour and is formed by calcination at high temperatures. According to the published literature[12] the increase of the chemisorbed oxygen concentration after the irradiation of nickel oxide is directly proportional to the original oxygen concentration in the non-irradiated sample. Due to the low value of this concentration in the original samples practically no concentration changes by irradiation were observed in pure NiO (sample No 15) and only a negligible increase was found in samples with the nickel oxide excess. The concentration increase of the ionogenic form of oxygen is due to the shift of the equilibrium between various forms in favour of the strongly bound chemisorbed form. In the other part of the series with the excess of U_3O_8 the observed increase of the surface oxidation ability after irradiation is due to the radiation oxidation of the U^{4+} ions

TABLE II

Oxidation ability of the surface expressed by the wt.% of O^{2-} in the mixed NiO–U_3O_8 oxides (A), the same quantity for samples irradiated by gamma rays (B), and the oxidation ability of the non-irradiated (A′) and irradiated (B′) samples taken per unit surface area (g O^{2-}/m^2)

Sample	$A . 10^{-3}$	$A' . 10^{-5}$	$B . 10^{-3}$	$B' . 10^{-5}$
1	5·3	2·8	76·1	40·3
2	3·6	2·8	66·9	51·9
3	2·9	1·5	13·2	6·8
4	2·9	1·6	9·0	5·0
5	3·1	1·4	16·5	7·3
6	4·3	1·0	14·4	3·5
7	5·1	1·0	14·7	2·9
8	7·1	1·3	19·4	3·5
9	8·0	1·3	17·9	2·9
10	9·2	0·9	32·9	3·3
11	10·4	1·1	26·6	2·9
12	14·3	1·6	35·9	4·0
13	12·8	1·4	34·9	3·7
14	11·6	2·3	22·2	4·3
15	8·7	5·3	8·2	5·0

which increases the concentration of U^{6+} ions. An analogous process has been proved in the study[13] on the gamma irradiation of uranium dioxide on air with the dose of 1 MGy.

The mutual interaction of both components manifests itself also on the starting temperature of the reduction which changes in dependence on the composition. Beginning with the sample No 6 (about 30 wt.% of NiO) the reduction proceeds with a measurable rate already at 350°C while the reduction of the sample No 1 (pure U_3O_8) started only at 470°C. According to various authors the reduction onset temperature of this oxide lies in a very broad interval from 400 to 900°C and it depends rather substantially on the preparation conditions and on the oxide genesis[14]. In the case of the sample No 1 the reduction degree increased exponentially with the amount of the oxide. As far as the process is strongly exoergic, thicker layers (higher amounts) of the oxide can be locally overheated and the actual temperature inside the sample can increase. In such centers the reaction initiation is much easier. In thinner layers similar centers are not formed due to a much faster heat transfer in the gas flow.

The character of the time dependence of reduction is also a function of the composition. From Fig. 3 (curve 2) it follows that the reduction of pure U_3O_8 proceeds with a high initial rate which continuously decreases to the reduction degree $\alpha \approx 0{\cdot}3$ In the interval $\alpha = 0{\cdot}3 - 0{\cdot}65$ the rate is constant and the final period of the process is again accompanied by a continuous decrease of the rate. The first period of the rate decrease corresponds to the reduction step $U_3O_8 \rightarrow UO_{2.59}$. The oxide of this stoichiometry represents the lowest limit of the existence of the U_3O_{8-x} phase at the temperature of 560°C (*cf.*[15]). The period with the constant rate corresponds to further reduction in the composition interval $UO_{2.59} \rightarrow UO_{2.25}$, ($U_4O_9$) when two phases U_3O_{8-x} and U_4O_9 coexist in the system[1]. According to the paper[5] the constant reduction rate is given by the constant presure of oxygen which is at the given temperature in equilibrium with both phases. Other authors explain this period with constant rate by the chemisorption of hydrogen as the rate-determining step[16] or by the similarity of the physical properties of both coexisting phases[17]. The final reaction step is characterized by the process $UO_{2.25} \rightarrow UO_{2+x} \rightarrow UO_2$. The rate decrease is probably caused by the blocking of the reaction interphase of $UO_{2.25}$ by the layer of newly formed UO_{2+x} phase and by the more difficult transfer of hydrogen to the interphase. In the series of uranium oxides of various stoichiometry all are n-type semiconductors except of uranium dioxide which forms solid solutions with oxygen (of the type UO_{2+x}, where x depends on the temperature). The concentration of positive holes, which recombine with free electrons, increases with the formation of this *p*-semiconductor phase. This mechanism can also decrease the overall reaction rate. The stoichiometry of the reduction product at temperatures >500°C of the sample No 1, calculated from the thermogravimetric data, corresponds to the oxide $UO_{2.06}$.

The period of constant rate becomes shorter and finally disappears as the content of nickel oxide in the sample increases. In the region of the component ratio 1 : 1 and in the excess of nickel oxide the reduction rate has a single maximum at $\alpha \sim 0{\cdot}3$ and proceeds by a characteristic autocatalytic dependence typical for the reduction of NiO (Fig. 3, curve *1*). From the reduction rate dependence on the composition (Fig. 4) it is evident that pure nickel oxide is reduced faster than mixed samples of any composition. A low per cent admixture of U_3O_8 decreases sharply the reduction rate of nickel oxide. In the region of the excess of the other component the reduction rate increases with the increasing content of nickel oxide and simultaneously the induction period becomes shorter. Under the assumption that the donor-type chemisorption of hydrogen on the surface is the rate-determining step of the U_3O_8 reduction[16] it may be expected that the addition of nickel oxide as a *p*-type semiconductor increases this chemisorption and therefore also the reaction rate. In the region of about 20 wt. per cent of NiO the presence of the stoichiometric compound indicates a high interaction of both components and an effect on their electronic configuration. Reduction connected with a crystallochemical transformation can be in this case also accelerated by a higher concentration of lattice defects, *i.e.*, by vacancies in the oxygen sublattice resulting from the substitution of U^{4+} ions in U_3O_8 by Ni^{2+} ions. On the other hand the process is retarded by the reduction decomposition of the mentioned relatively stable compound. The rate increase in this region is therefore rather inconspicuous (Fig. 4) and only with the further increase of the nickel

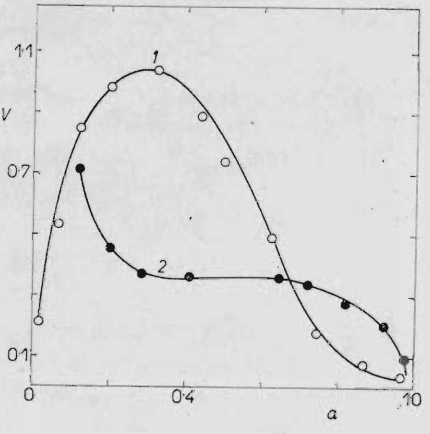

FIG. 3

Reduction rate V (mg/min) as a function of the reduction degree. *1* sample No 8 (380°C), *2* sample No 1 (560°C)

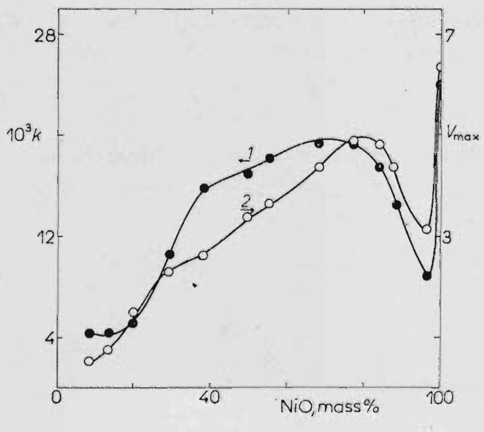

FIG. 4

Dependence of k (in relative units) and of V_{max} (mg/min) on the composition. Reduction temperature 410°C. *1* k, *2* V_{max}

oxide content the reduction rate sharply increases. The described behaviour, together with the shortening of the induction period, indicate that (metallic) nickel formed by the reduction also catalytically increases the reduction rate of the other component. Moreover, also the concentration of uranium dioxide that is not reduced further and that hinders the active interphase decreases with the increasing content of nickel oxide. Similarly as in several other two-component systems based on nickel oxide[11] the dependence of the reaction rate on the composition is characterized by a maximum in the broad vicinity of the center of the series. In this region the system has the maximum dispersity of microcrystallites (Table I) and also of the grains (Fig. 1), high specific surface area and therefore also the best contact of both components and a high concentration of defects. From the dependence $v = f(\alpha)$ (Fig. 3) it is evident that the reduction kinetics of this system, in which both components form an independent phase, is determined already in the center of the series by the reduction of nickel oxide which is thermodynamically the easier reducible component. In samples with a high excess of NiO (>90 wt.%) the observed increase of the lattice parameter of NiO by a small addition of U_3O_8 (samples No 13 and 14) indicates the formation of a homogeneous solid solution. The incorporation of U_3O_8 as a n-type semiconductor in the given concentrations sharply decreases the reduction rate of nickel oxide. Fig. 4 shows the qualitatively similar dependence of both maximum reduction rate and rate constant on the composition of mixed oxides. In the excess of U_3O_8 these dependences can be correlated with the changes of the apparent activation energy (E_a) of the reduction. Sample No 1 (pure U_3O_8) is characterized by the value $E_a = 180$ kJ/mol which increases up to 310 kJ/mol in the region of the stable compound of both components (up to about 15 wt.% of NiO). With the increasing content of NiO up to about 50 wt.% E_a decreases again to 150 kJ/mol and is further practically independent of the composition. The conspicuous change of the nickel oxide reduction rate with the addition of the other component is connected with the changes of the pre-exponential factor. The higher value of the activation energy of the pure nickel oxide reduction in comparison with the published data (90–100 kJ/mol)[18] is evidently given by the high stoichiometry of this oxide which is under identical conditions reduced more slowly than the non-stoichiometric black oxide prepared by the decomposition of salts at temperatures below 500°C (*cf.*[7]). In agreement with the specific genesis of nickel oxide the reduction kinetics of mixed oxides (pure NiO inclusive) can be quantitatively expressed by the modified Prout–Tompkins equation[9] $(0{\cdot}3 + \alpha)/(1 - \alpha) = e^{kt}$ in the interval of $\alpha \sim 0{\cdot}05 - 0{\cdot}80$. The reduction of pure U_3O_8 can be described in agreement with the published studies[19] by the equation derived from the contracting sphere model of the solid phase decomposition, $1 - (1 - \alpha)^{1/3} = kt$. In these two relations α is the reduction degree in the time t and k is the rate constant.

The interaction of both components of the system manifests itself also in the dependence of the secondary reduction kinetics on the composition. This process has been studied in the temperature interval 380–500°C so that the primarily reduced samples were oxidized in the air flow to a constant degree and then secondarily reduced by hydrogen at the same temperature. The primarily reduced sample No 15 (pure NiO) is oxidized slowly and only to a low degree (about 30%). Oxidation proceeds only in the surface layers and is hindered by a relatively compact layer of the oxide on the surface of the grain. Both the degree of oxidation and the oxidation rate increase with the increasing content of uranium. The oxidation of pure UO_2 is limited – due to the high mobility of oxygen in the lattice[5] – by the diffusion of oxygen and under these conditions it proceeds quantitatively. On the other hand the secondary reduction rate decreases with the increasing content of uranium. Also the degree of the secondary reduction, related to the content of the respective oxide formed by oxidation, decreases with the increasing content of U_3O_8. Assuming that oxides of the stoichiometry NiO and U_3O_8 are the products of the oxidation, the rapid reduction of the nascent NiO (sample No 15) proceeds quantitatively and the slower reduction of U_3O_8 (sample No 1) – due to a higher affinity of uranium to oxygen – proceeds only to $\alpha \sim 0{\cdot}8$. However, even in this case the secondary reduction rate of the nascent oxide is higher than the rate of the primary process. In mixed-oxide samples the degree of secondary reduction exceeds in the whole composition range the theoretical value corresponding to the reduction of oxides of the given stoichiometry. From this fact and also from the analysis of the oxidation kinetics the interaction of both components can be deduced. Oxidation of uranium dioxide proceeds under the given conditions only to the oxide of the stoichiometry U_3O_8. In the mixed system, however, the oxidized UO_2 makes the oxidation of nickel to the oxide, the stoichiometry of which corresponds to $NiO_{1.18}$ in samples with a high content of nickel, more easier. The oxidation of both components proceeds as parallel reactions. In the secondary reduction the catalytic effect of the reduced nickel on the reduction of U_3O_8 is completely analogous as in the primary reduction.

The effect of preliminary irradiation on the reduction kinetics of mixed oxides is given in Fig. 5, presenting the dependence of Δk on the composition. This quantity is defined as $\Delta k(\%) = (k^+ - k)/k \,.\, 100$, where k^+ is the reduction rate of the irradiated sample and k characterizes the reduction rate of the initial sample at the same temperature. From this dependence it is evident that the effect of pre-irradiation is negative (the reduction rate decreases) in the region of U_3O_8 excess. It continuously changes into a positive effect in samples with an excess of the other component. With the increasing reduction temperature this effect remains practically unchanged in the first region while in the region of NiO excess Δk conspicuously decreases and at about 440°C Δk for the reduction of mixed oxides becomes negative. From the graph it is evident that the maximum negative effect is observed in samples with a high excess of U_3O_8 and that the effect of pre-irradiation is negligible ($\Delta k \approx 0$) in both extreme regions of composition where there is a transition of the homogeneous system into a binary system if the concentration limit of the minor component is exceeded. Due to the higher temperature stability of this effect in samples with the excess of uranium it may be assumed that the negative effect of irradiation is a consequence of chemical changes in the system. From the comparison of the reduction degrees of the non-irradiated and irradiated samples it turns out that the irradiation on air leads to the surface radiation oxidation accompanied by chemisorption of oxygen (Table II). The reduction rate of the original oxide U_3O_8 is then retarded by the parallel reduction of the more stable higher oxide and by the slowing down of the hydrogen adsorption. With the increasing content of nickel oxide in samples the change of the adsorption properties of the surface induced by irradiation becomes the rate-determinig factor. The concentration decrease of the ionogenic superstoichiometric oxygen is connected with the increase of the rate of donor processes – of the hydrogen adsorption and of the reduction rate. In the whole range of the binary system the concentration of chemisorbed oxygen (B′) is practically constant (Table II). From the temperature dependence of this effect it follows that the substantial increase of the reduction rate is caused by the reaction centers, particularly by the stabilized non-equilibrium charge defects or by the lattice defects generated by the radiation. Their concentration increases with the increasing interaction between the two component determined by their dispersion degree. The maximum of the radiation effect lies therefore in the region of the maximum reduction rate of non-irradiated mixed oxides (Fig. 4). The change of the reaction centers concentration induced by irradiation is also indicated by the fact that the activation energy of reduction of the modified samples remains practically unchanged if compared with the reduction of the original mixed oxides.

The irradiated samples with a high content of nickel oxide in the homogeneous region (pure nickel oxide inclusive) are also reduced with higher rate than the original oxides ($\Delta k > 0$). In this region the donor-type adsorption process determined by the

FIG. 5

Dependence of Δk (%) on the composition. Reduction temperature 380°C genesis of nickel oxide is again the rate-determining process. Because the Fermi level of the oxide prepared by the low-temperature calcination (below 500°C) lies close to the valence band, its shift towards higher values by the gamma irradiation decreases the reduction rate as it has been proved in a series of papers[19,20]. In oxides prepared by calcination at high temperatures the Fermi level is close to the conduction band and its shift towards higher values increases the reduction rate[21], again in agreement with the experimental results.

REFERENCES

1. Zhukovskii V. M., Vlasov V. G.: Kinet. Katal. *5*, 76 (1964).
2. Shalaginov V. N., Vlasov V. G., Charov I. V.: Zh. Prikl. Khim. *41*, 1397 (1968).
3. Vlasov V. G., Pismenko V. T., Larin A. A.: Zh. Prikl. Khim. *41*, 2640 (1968).
4. Vlasov V. G., Pismenko V. T., Larin A. A.: Kinet. Katal. *9*, 1094 (1968).
5. Heynen H. W. G., Camp-van Berkel G. M. M., van der Baan H. S.: J. Catal. *48*, 386 (1977).
6. Markov V. K.: *Uran, Metody ego Operedeleniya*, p. 151. Atomizdat, Moscow 1964.
7. Pospíšil M., Cabicar J., Rejholec V.: This Journal *35*, 1319 (1969).
8. Brise C.: Ann. Chim. (Paris) *53*, 325 (1963).
9. Bond W. D.: J. Phys. Chem. *66*, 1573 (1962).
10. Pospíšil M., Tvrzník M.: This Journal *43*, 998 (1978).
11. Pospíšil M., Topinka J.: This Journal *45*, 1754 (1980).
12. Maxim I., Braun T.: J. Phys. Chem. Solids *24*, 537 (1963).
13. Gromov V. V.: *Vliyanie Ioniziruyushchevo Izlucheniya na Kinetiku Rastvoreniya Tverdykh Tel*, p. 107. Atomizdat, Moscow 1976).
14. Imriš P.: Report ÚJV ČSAV No 960, Řež near Prague 1964.
15. Gronvold F.: J. Inorg. Nucl. Chem. *1*, 357 (1955).
16. Notz K., Mendel M. G.: J. Inorg. Nucl. Chem. *14*, 55 (1960).
17. Vlasov V. G., Semovin J. N.: Zh. Prikl. Khim. *40*, 374 (1967).
18. Frety R., Tournayan L., Charcosset H.: Ann. Chim. (Paris) *9*, 341 (1974).
19. Ukazi R.: J. Atom. Energy Soc. Jap. *2*, 117 (1960).
20. Yamashina T., Nagamatsuya T.: Bull. Chem. Soc. Jap. *38*, 507 (1965).
21. Gisquet E., Destrian M.: Bull. Soc. Chim. Fr. *5*, 1455 (1969).

Translated by Z. Prášil.