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## EFFECT OF IONIZING RADIATION ON THE KINETICS OF REDUCTION OF NiO-MgO MIXED OXIDES WITH HYDROGEN

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The low-temperature reduction of the mixed system nickel oxide-magnesium oxide with hydrogen was studied thermogravimetrically in the region 260–470°C. The two oxides form in the whole composition region solid solutions, some physicochemical parameters of which vary nonmonotonically with the sample composition. The kinetics and degree of reduction of nickel oxide are appreciably affected by the presence of the unreduced magnesium oxide, in higher concentrations lowering the reaction rate. The kinetics of the reduction can be quantitatively described by the equation  $1 - (1 - \alpha)^{1/3} = kt$ , valid in dependence on the composition in differently wide ranges of the degree of reduction  $\alpha$ . The reaction rate can be varied, particularly for samples with low contents of magnesium oxide, by heat treatment in inert atmosphere at 700°C, and for all samples by irradiation by gamma rays or fast neutrons. The reduction rate grows with the increasing content of magnesium oxide up to a constant value. The positive effect increases with the increasing gamma dose and, according to the kind of radiation, in the order  $\gamma, n$ . The variation of the reactivity of irradiated or thermally treated mixed oxides is due predominantly to the shift of the equilibrium of the lattice defects, formation and stabilization of new centres, which affect the rate of nucleation of the forming metal phase.

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In the previous works, dealing with the kinetics of reduction of two-component mixed oxides based on nickel oxide, the properties of this oxide were altered by the other component possessing the *p*- or *n*-semiconductive nature<sup>1-3</sup>. The mutual interaction of the two oxides manifested itself in the marked dependence of the reaction rate on the composition, although the two components usually did not form a solid solution at all<sup>2</sup> or only in a limited composition region<sup>4</sup>. It appeared therefore interesting to examine the reduction of a two-component system of the type nickel oxide – insulator, where the two oxides form a homogeneous solid solution in the whole concentration region 0–100% of a component. For this was chosen the system nickel oxide-magnesium oxide, which after the reduction affords a frequently employed hydrogenation catalyst Ni on a support<sup>5</sup>. The reduction of this system has not been practically studied. In the work<sup>6</sup> the reduction of the system of cobalt monoxide with magnesium oxide has been investigated and a rather complex mechanism of interaction of the two oxides, changing with the composition, has been inferred.

Based on several tentative experiments, an analogous behaviour is assumed also in the case of the system investigated in the present work. The conditions of preparation of the mixed oxides, the composition region (up to 10 mol % MgO) and the reduction temperature region (600–1000°C) applied in the work<sup>6</sup> are, however, quite different from those used by us. We were in addition concerned with the study of the prior irradiation by <sup>60</sup>Co gamma rays and by fast neutrons from a <sup>252</sup>Cf source on the kinetics of reduction of the mixed system nickel oxide–magnesium oxide.

## EXPERIMENTAL

The mixed oxides of different compositions were prepared by calcination of the basic carbonates obtained by coprecipitation from solutions of nitrates of the two metals with a potassium carbonate solution in a 15% excess with respect to the stoichiometry (chemicals reagent grade purity, concentration of all the solutions 1 mol/l). The precipitates were filtered out, repeatedly decanted, and washed till a negative reaction for nitrates, and dried at 120°C for 3 h; then they were calcinated in an electric resistance furnace at 600°C on air for 6 h. In the case of two of the samples, additional portions were calcinated also at 400°C and 800°C in otherwise identical conditions. After grinding in an agate mortar the fraction grain size 0.05–0.25 mm was selected. The content of the two metals in the samples was determined complexometrically. The specific surfaces were measured *via* adsorption of nitrogen at low temperatures. The microstructure of the mixed oxides was studied by the Debye–Scherrer and the back beam methods. From the half widths of the diffraction lines, the size of the coherent regions of the samples was calculated. The content of the overstoichiometric oxygen was determined iodometrically. The morphology of the samples was studied on a scanning electron microscope JSM-50 (Jeol). The samples were divided into several portions: the first one was gamma irradiated from a cobalt source by an applied dose  $D_{\gamma_1} = 1.09 \cdot 10^6$  Gy, the second one was also gamma irradiated, by the dose  $D_{\gamma_2} = 4.9 \cdot 10^6$  Gy and the third portion was irradiated by fast neutrons in a source with <sup>252</sup>Cf (Amersham) of the fluence  $3.188 \cdot 10^{17}$  n/m<sup>2</sup> (applied dose  $D_n = 1.3 \cdot 10^3$  Gy). The reduction of the mixed oxides was examined in the temperature region 260–470°C in identical experimental conditions for the initial oxides as well as for the prior irradiated samples. The kinetic of the reduction was studied thermogravimetrically on the apparatus described previously<sup>1</sup>. From the preliminary experiments the conditions were found where the rate and the time course of the reduction did not depend for a standard batch of 50 mg on the hydrogen flow rate for any composition of the sample. This region was for the arrangement used ensured at the flow rate 60 ml/min, applied during all experiments. The sample designation, their composition, specific surfaces, and size of the coherent regions are summarized in Table I.

## RESULTS

It follows from the results of the analysis (Table I) that the standard temperature of the decomposition of the basic carbonates (600°C) yields a mixture of nickel oxide and magnesium oxide which in the sum of the weight percentages do not attain 100%. In samples prepared by calcination at 800°C the decomposition is virtually complete, in the other samples the presence of nondecomposed carbonates was found by IR spectroscopy. The microstructural analysis only revealed the presence of the two

oxides possessing the cubic structure, which in accordance with the published data<sup>7</sup> form substitution solid solutions in the whole composition region; this follows also from the study of the morphology of the mixed oxides (Fig. 1\*) and its change by the reduction (Fig. 2\*). A two percent addition of the non-reducible component (MgO) does not constitute a separate phase in the system after the reduction nor does it stabilize the cubic structure of the nickel reduced. In comparison with the original mixed oxide (Fig. 1\*), the dispersity and the specific surface decrease down to 20% of the original value. Similarly changes the morphology of the samples after an hour's heat treatment in inert atmosphere at high temperatures or that of oxides prepared by calcination at high temperatures. These processes are accompanied by an increase of the degree of aggregation of the individual grains and perhaps sintering

TABLE I

Composition, Specific Surface ( $S$ ), and Size of the Coherent Regions ( $L$ ) of the NiO-MgO Mixed Oxides

Sample No	Wt. %					Mol %		$S$ m <sup>2</sup> /g	$L$ nm
	Ni	Mg	NiO	MgO	NiO + MgO	NiO	MgO		
1	76.27	—	96.86		96.86	100	—	11.1	51.1
2	74.65	1.16	94.81	1.93	96.74	98.00	2.00	9.77	92.2
3	73.08	1.63	92.81	2.71	95.52	97.12	2.88	15.3	44.3
4	66.74	5.08	84.76	8.43	93.19	90.95	9.05	16.7	—
4 <sup>a</sup>	67.85	5.00	86.17	8.31	94.48	91.20	8.80	29.0	21.8
4 <sup>b</sup>	69.57	5.37	88.36	8.92	97.28	90.83	9.17	1.9	—
5	61.97	9.06	78.70	15.05	93.75	83.96	16.05	17.5	37.3
6	53.50	15.37	67.94	25.52	93.46	71.76	28.24	23.2	24.7
7	43.40	24.18	55.10	40.10	95.20	57.90	42.10	37.3	25.4
8	31.98	31.89	40.61	59.96	94.57	43.40	56.60	59.5	15.4
9	23.08	36.57	29.31	60.70	90.01	32.56	67.44	60.6	18.2
10	20.03	39.07	25.43	64.86	90.29	28.17	71.83	109.3	16.5
10 <sup>a</sup>	17.29	37.97	21.95	63.02	84.97	25.84	75.16	110.5	14.4
10 <sup>b</sup>	25.07	43.29	26.16	71.86	98.02	26.70	73.30	16.3	—
11	7.34	49.52	9.32	82.21	91.59	10.19	89.81	59.7	17.7
12	1.04	54.61	1.33	90.60	91.93	1.44	98.56	61.6	16.7
13	—	56.32	—	93.49	93.49	—	100	28.6	30.7

<sup>a</sup> Calcinated at 400°C; <sup>b</sup> calcinated at 800°C.

\* See insert facing p. 1026.

of the aggregates (Fig. 2\*) and stabilization of the clusters. The lowering of the specific surface is particularly appreciable in the region of excess nickel oxide. As the content of magnesium oxide grows, its structure stabilizing effect also increases, both for the original mixed oxides and for the samples after the reduction. The irradiation of the mixed oxides by the doses applied has no effect upon the specific surface value.

As follows furthermore from Table I, the specific surfaces depend markedly non-monotonically on the composition, and the coherent region size of the cubic structure varies in the regions of excess of one or the other component. The amount of the ionogenic overstoichiometric oxygen decreases nonmonotonically with the increasing content of magnesium oxide (Table II) and drops down to zero in samples containing magnesium oxide in high excess. The same shape possess these dependences for the samples irradiated by the lower dose of the gamma radiation ( $D_{\gamma_1}$ ) or fast neutrons. The amount of oxygen chemisorbed on the irradiated samples is, however, higher as compared with the initial samples, this effect increasing with the increasing content of magnesium oxide. An enhanced oxygen chemisorption occurs also on samples thermally treated up to 500°C and particularly on samples prepared by high-temperature calcination at 800°C (Table II). Neither the heat treatment nor the irradiation in the aforesaid conditions brings about microstructural changes.

At the lowest temperature applied, 260°C, the reduction proceeds with a measurable rate only in the case of the first two samples of the series (Table I). At 470°C the mixed

TABLE II

Amount of the Chemisorbed Oxygen Normalized to the Unit Surface ( $10^{-5} \text{ g}_{\text{O}_2} / \text{m}^2$ ) for the Initial NiO-MgO Mixed Oxides (A) and the Same Samples after their Irradiation by the Lower Dose of Gamma Rays (B) and by Fast Neutrons (C)

Sample No	A	B	C	Sample No	A	B	C
1	3.6	3.3	3.2	8	0.032	0.26	0.14
2	1.53	1.9	1.2	9	0.009	0.11	0.04
3	3.05	2.14	1.9	10	0.004	0.04	0.02
4	1.35	1.58	4.2	10a	0.52	—	—
4a	7.81	—	—	10b	1.30	—	—
4b	15.7	—	—	11	0	0	0
5	0.63	0.91	1.9	12	0	0	0
6	0.69	1.24	0.9	13	0	0	0
7	0.099	0.22	0.20				

\* See insert facing p. 1026.

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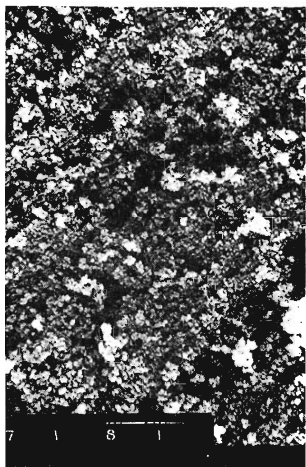


FIG. 1  
Morphology of the Sample No 2 (Table I)  
Electron scanning microscope, magnification  $10^4\times$ ; the line segment indicated corresponds to  $2\mu\text{m}$ .



FIG. 2  
Morphology of the Sample No 2 (Table I)  
after Reduction with Hydrogen  
Electron scanning microscope, magnification  $10^4\times$ .

oxides reduce up to the content 40.1 wt.% MgO (sample No 7), samples containing excess magnesium oxide do not reduce in the temperature interval applied with a measurable rate. The values of the relative degree of reduction ( $\alpha_{rel}$ ) were calculated from the comparison of the experimental weight losses during the reduction with the theoretical ones; the latter were calculated according to the weights and compositions of the samples assuming that the nickel oxide reduction proceeded completely. As can be seen from Fig. 3, the degree is at the given temperature a function of the composition and starting from the sample No 2 decreases continuously with the increasing content of magnesium oxide. Only in the region of high excess of nickel oxide the  $\alpha_{rel}$  values are in a wide temperature interval (380–470°C) virtually equal and independent of the temperature. This dependence thus bears out the assumption that in the system in agreement with the thermodynamic properties of pure magnesium oxide, only nickel oxide is reduced, this reduction being in the conditions used only partial. The degree of reduction varies only slightly with the temperature and changes appreciably with the sample composition.

The kinetics of reduction of the mixed nickel and magnesium oxides can be quantitatively described by the equation  $1 - (1 - \alpha)^{1/3} = kt$ , where  $\alpha$  is the degree of reduction in the time  $t$  and  $k$  is the rate constant. For the samples containing excess nickel oxide (except for pure nickel oxide, sample No 1) this relation is obeyed in the relatively narrow region of  $\alpha = 0.05 - 0.6$ . As the content of magnesium oxide increases the upper limit of this region shifts up to  $\alpha = 0.9$ . From the temperature dependences of the rate constants the values of the apparent activation energy of reduction were calculated. They lie in the region  $(5.8 - 10.2) \cdot 10^4$  J/mol except for the samples with low contents of magnesium oxide, where the activation energy is considerably lower –  $3.6 \cdot 10^4$  and  $2.5 \cdot 10^4$  J/mol for the samples No 2 and 3, respectively; higher values were obtained for the samples with higher contents of magnesium oxide.

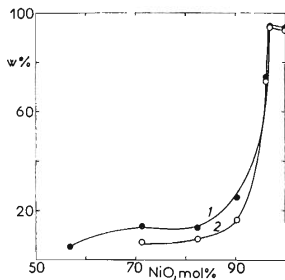


FIG. 3  
Dependence of the Relative Degree of Reduction (%) on the Composition  
1 470°C; 2 380°C.

The effect of the composition on the reaction rate is shown in Figs 4 and 5; the dependences of the maximum rate of the reduction (Fig. 4) and of the rate constant (Fig. 5) on the composition are seen to possess qualitatively the same shape. If small additions of magnesium oxide are applied (sample No 2), the reduction rate is relatively high, and drops virtually exponentially with the increasing content of magnesium oxide in the sample, particularly at high temperatures (Fig. 5, curves 1 and 2). The same dependence on the composition is found for both quantities,  $v_{\max}$  and  $k$ , normalized to unit particle size (Table I). The maximum of the rate is, however, shifted towards the sample No 3, which also contains a small amount of magnesium oxide and in its composition approaches the sample No 2.

The mixed oxides of various compositions were also reduced at 380°C after prior heat treatment in nitrogen atmosphere at 300–700°C for 1 h. The low-temperature treatment, up to 500°C, affects virtually neither the rate nor the degree of reduction. The reduction of the sample No 2 thermally treated at 700°C proceeds with twice as high rate in comparison with the original mixed oxide. In the case of the other samples treated in the same manner the reaction rate is lower and decreases with the increasing magnesium oxide content. Generally, the effect of the temperature of calcination during the preparation of the oxides is much more pronounced than that of their successive heat treatment. The sample No 4b (Table I) is not reduced with a measurable rate at 380°C.

The reduction of the irradiated mixed oxides was examined in the temperature region 290–350°C. The effect of irradiation on the reaction rate is shown in Fig. 6,

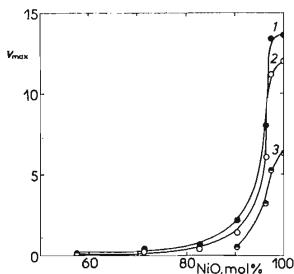


FIG. 4

Dependence of  $v_{\max}$  ( $\text{mg min}^{-1}$ ) on the Composition

Temperature of reduction: 1 470°C; 2 440°C; 3 350°C.

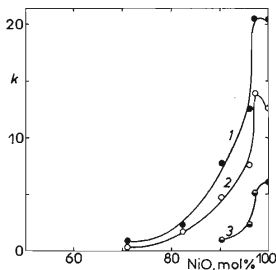


FIG. 5

Dependence of  $k$  ( $\text{min}^{-1}$ ) on the Composition

Temperature of reduction: 1 470°C; 2 440°C; 3 350°C.

where the quantity  $\Delta = [(k^+ - k)/k] \cdot 100 (\%)$  is plotted in dependence on the composition of the samples reduced at 320°C; here  $k^+$  and  $k$  are the rate constants of the irradiated and unirradiated samples, respectively. The irradiation by fast neutrons is seen to have a positive effect (acceleration of the reaction), increasing with the content of magnesium oxide. Similarly is affected the kinetics of reduction of the samples irradiated by the higher dose of gamma radiation ( $D\gamma_2$ ) save pure nickel oxide, where a slight negative effect (lowering of the reaction rate) appears. Application of the lower gamma dose ( $D\gamma_1$ ) leads to a negative effect in the region of excess nickel oxide; otherwise the shape is analogous as in the preceding case. The magnitude of the positive effect decreases for the individual cases in the order  $n > D\gamma_2 > D\gamma_1$ . In the case of the samples irradiated by neutrons and the higher gamma dose the degree of reduction was observed to increase in average by 7% with respect to the unirradiated oxides. Except for pure nickel oxide, the reduction of the neutron-irradiated mixed samples is associated with a lowering of the activation energy to approximately half its original value. The gamma-irradiated samples are reduced with a slightly increased activation energy (approximately 25%) for both doses applied.

## DISCUSSION

As follows from the experimental results, the nickel oxide reduction is altered by the presence of non-reduced magnesium oxide. Although the two components form substitution solid solutions in the whole composition region, their mutual affecting appears in nonmonotonic dependences of the physicochemical parameters examined on the composition. The changes of the specific surfaces are associated with the size and morphology of the crystallites of the samples of different composition, which

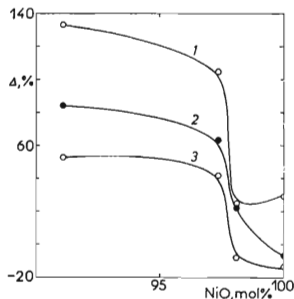


FIG. 6  
Dependence of  $\Delta$  (%) on the Composition  
Temperature of reduction 320°C. Irradiation: 1  $n$ ; 2  $D\gamma_2$ ; 3  $D\gamma_1$ .



change markedly particularly in the two limiting regions of the series. As the content of the minor component grows up to a certain concentration, its aggregation takes place and clusters are formed<sup>8</sup>. In the regions of higher concentrations the formation of new clusters may be competed by another process — growth of the existing aggregates. The increase of the surface of the samples prepared by calcination at lower temperatures can be attributed to the presence of non-decomposed amorphous carbonates, regarding the proved decrease of the specific surfaces in the genetic series<sup>9</sup> starting salt  $\xrightarrow{\text{(calcination)}}$  oxide  $\xrightarrow{\text{(reduction)}}$  metal. In mixed oxides obtained by calcination at 800°C the lowering of the surface is a result of the sintering processes, particularly in the region of excess nickel oxide.

As follows from Table II, the amount of the ionogenic overstoichiometric oxygen relative to a unit surface area decreases discontinuously with the increasing content of magnesium oxide. With regard to the *p*-semiconductive characteristics of nickel oxide it can be assumed — in accordance with the electronic theory — that only this oxide is the carrier of the chemisorbed oxygen. According to the published data the chemisorption of oxygen on magnesium oxide is negligible and even a high-temperature heat treatment (1300°C) in oxygen atmosphere does not bring about formation of impurity levels in the forbidden band<sup>10</sup>. The fact that the amount of overstoichiometric oxygen relative to unit amount of nickel also decreases with the increasing magnesium oxide content gives another evidence of the negative effect of the latter on the oxygen chemisorption. This decrease, which is in contrast to the results of the work<sup>11</sup>, can be explained in terms of the electric properties of magnesium oxide conditioned by the preparation procedure. In the case of mixed nickel oxide–magnesium oxide solid solutions, a weak semiconductivity has been observed in some instances<sup>12</sup>, as a consequence of the incorporation of nonstoichiometric magnesium oxide and formation of donor levels of overstoichiometric magnesium. In such system the rise of the oxygen chemisorption — as an acceptor process — with the increasing content of magnesium oxide is in full agreement with the electronic theory of adsorption on semiconductors. In the system under study, the purely dielectric nature of magnesium oxide was proved experimentally. The cause of the nonmonotonic decrease of the amount of chemisorbed oxygen with the growing content of magnesium oxide may lie in the above-discussed morphological differences between the samples of different compositions with the associated different interaction of the electronic structures of the two components in the various composition regions. The possible nonuniform distribution of the Ni<sup>2+</sup> ions on the surface and in the bulk of the mixed oxide should be also taken into consideration. The sample irradiation brings about an enhanced oxygen chemisorption, increasing with the growing magnesium oxide content. In the region of excess nickel oxide the determining phenomenon is the shift of the equilibrium of the various forms of sorbed oxygen in favour of the strongly adsorbed ionogenic form, observed for pure nickel oxide<sup>13</sup> and other binary systems involving nickel oxide<sup>2,14</sup>. As the content of magnesium

oxide increases, the irradiation results probably in an increase of the concentration of the donor centres either directly at magnesium oxide, or in the capture of nonequilibrium electrons at the  $\text{Ni}^{2+}$  ions; thereby the chemisorption of oxygen on the surface of the mixed oxide increases.

Figs 3 to 5 show the generally negative influence and strong retarding effect of magnesium oxide on the rate of reduction of nickel oxide. The continuous decrease of the rate as well as of the degree of reduction with the increasing content of magnesium oxide corroborates the highest degree of the mutual interaction of the two components conditioned by the formation of the solid solution. In contrast to heterogeneous systems, the magnesium oxide incorporated does not thus confine itself to a mere blocking of the reaction interface, but directly alters the lattice structure and defects and thereby the reactivity of the solid phase. The affecting of the kinetics of the reduction by the various physicochemical parameters, which change discontinuously with the composition, is in these circumstances virtually negligible. This is borne out also by the quite analogous shapes of the dependences of the quantities  $v_{\max}$  and  $k$  normalized to the unit particle size on the composition. The fact that a low-percentage addition of magnesium oxide brings about acceleration of the reaction rate, appearing particularly at high temperatures (Fig. 4), can be explained — in accordance with the results of the work<sup>6</sup> — by the action of at least two mutually opposite processes. As the concentration of the magnesium oxide incorporated increases, the concentration of the cation vacancies in nickel oxide lowers, whereby the equilibrium of the lattice defects is shifted. As a consequence, the rate of the reduction drops, and for a sufficiently high magnesium oxide content the effect approaches the saturation state (Fig. 4). In the opposite direction is the reaction affected by the deformation and strain in the nickel oxide lattice, which obviously also weakens the strength of the Mg-O bond. This facilitates the nucleation associated with a rise of the reaction rate and lowering of the activation energy. The effect only manifests itself in the region of low concentrations of magnesium oxide during the whole reaction course, with its increasing content the effect is confined to the initial reduction stage and as early as the medium stage the rate is determined by the negative process. This is corroborated by the relatively high initial reduction rates for samples with high contents of magnesium oxide and the slow reaction course particularly in the final stage, associated with low values of the degree of reduction attained (Fig. 3). Regarding the values of the apparent activation energy of the reaction and the pronounced dependence of the positive effect on the temperature (Fig. 5), it can be further assumed that the rate-controlling step is the diffusion within the solid. The rate of reduction was found experimentally to increase on the high-temperature heat treatment in inert atmosphere. Since the positive effect of the heat treatment only shows up in the region of low magnesium oxide contents, it can be also associated with the structure changes and lattice defects. The cause of the thermal activation can be a rapid recrystallization process and increase of the concentra-

tion of the active centres (or activation of the existing centres) as a result of the contraction and removal of the lattice microstrain<sup>4</sup>. The positive effect is opposed at high temperature by the sample sintering associated with a reduction of the surface area. This process, however, only manifests itself by a lengthening of the induction period, or – at low temperatures of reduction – by a lowering of the initial reaction rate (up to  $\alpha \approx 0.03$ ).

As can be seen from Fig. 6, the gamma irradiation of the samples leads to a marked increase of the rate of reduction of the mixed oxides and to a negative effect on pure nickel oxide (or the sample No 2) in the case of the lower applied dose  $D_{\gamma 1}$ . As the dose increases, so does the positive effect, whereas the reverse is true of the negative effect. The shape of the dependence of the quantity  $\Delta$  on the composition agrees with the previous results<sup>3</sup> and gives evidence of the action of two competing processes. In nickel oxide-containing oxide samples the gamma-irradiation leads to a shift of the equilibrium between the various forms of the oxygen adsorbed in favour of the chemisorbed ionogenic form. Simultaneously, in the sense of the electronic theory, the rate of the donor reaction decreases, due to the lowered adsorption of the reducing hydrogen. The accelerating process is the formation of the charge or lattice defects, which become the adsorption and reaction centres. Their concentration grows with the increasing content of the other component up to a state of saturation. The critical region is again systems with low contents of magnesium oxide (about 2%), where the maximum increase of the  $\Delta$  quantity occurs in a narrow concentration range of its incorporation. The region is identical with that of the maximum drop of the reduction rate of the unirradiated mixed oxides (Figs 4 and 5). The shift of the equilibrium of the lattice defects resulting from the lowering of the concentration of the cation vacancies in nickel oxide on the addition of magnesium oxide and accompanied by the lowering of the reaction rate thus in this region not only is completely compensated for by the formation of the new radiation-induced defects and their stabilization in the lattice, but it ceases to be the determining factor. Inasmuch as the effect of irradiation on the overall reaction rate is a superposition of two mutually opposite effects and in addition to the existing centres newly generated ones occur as well, no pronounced change of the activation energy is to be expected, which conforms to the experimental results.

The assumption that the reactivity of the system under study is governed primarily by the concentration of the lattice defects, is borne out by the positive effect associated with the applied neutron irradiation of the samples. This irradiation results predominantly in the creation of point lattice defects and to a lower extent in the creation of charge perturbations by secondary ionization. The enhanced concentration of the active centres and formation of the new centres and the associated speeding up of the metal nucleation accelerate the reaction and lower its activation energy. In the case of some binary oxide systems irradiated by fast neutrons, a negative effect on the reaction rate has been observed in the region of excess nickel oxide<sup>3</sup>.

The lowering of the reactivity of the irradiated solid can be a result of the breakdown of the existing centres (the polishing effect of radiation), of the capture of the adsorption centres on the point defects formed, or other processes<sup>3</sup>. The effect of these phenomena can be assumed also in the system nickel oxide-magnesium oxide, where in the region of excess nickel oxide the effect is positive ( $\Delta > 0$ ), but not very pronounced (Fig. 6). The maximum rise of the reaction rate appears in the same narrow concentration range of the other component added (MgO) as in the case of the gamma-irradiated samples. The saturation of the effect occurs obviously at higher magnesium oxide content than in the preceding case. The assumption that the increase of the concentration of the relatively stable lattice defects, which facilitate the reduction and the nucleation, determines the positive effect of the irradiation, is in accordance with the experimentally found ascent of the effect in the order  $D\gamma_1 < < D\gamma_2 < D_n$  as well as with the increase of the degree of reduction for the samples irradiated by the higher gamma dose or by neutrons.

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