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Effects of genesis and ionizing radiation on the physicochemical properties and reduction reactivity of NiO–ZnO mixed oxides with hydrogen

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Abstract

The physicochemical properties and hydrogen reduction reactivity have been studied for two series of nickel and zinc mixed oxides of various compositions; the two series differ in the genesis of both their major components. It was found that the different absolute values of the physicochemical parameters of the mixed oxides vary with their compositions and depend on the origin of the major components. The changes in the properties of the samples in both series can be correlated with their reduction reactivity as seen by isothermal thermogravimetry in the temperature range 260–500 ° C.

Only the series containing zinc oxide in interaction with strongly non-stoichiometric nickel oxide appears to be sensitive to pre-irradiation by γ rays (328 kGy and 3.7 MGy doses) and accelerated electrons (500 kGy dose). The negative effect (a decrease in the rate of reduction) in the region of excess nickel oxide reverses to a positive one (acceleration of reduction) with increasing zinc oxide content, forming a separate phase of the mixed system.

INTRODUCTION

In previous papers [1,2], the effects of the genesis and conditions of preparation on the reactivity of various two-component oxide catalysts during their reduction with hydrogen have been systematically studied. Different physicochemical properties as well as differences in reduction kinetics were observed with nickel and zinc mixed oxides of various compositions prepared either by thermal decomposition of crystalline nitrates of both metals [3] or by calcination of coprecipitated basic carbonates [4]. When the same system contains an incorporated radionuclide, ^{65}Zn, a decrease or, in contrast, an increase in the reduction rate was found, with corresponding changes in apparent activation energy, depending on the specific activity of the samples [5].

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The aim of the present work was to investigate the physicochemical properties of two analogous systems of mixed inverse genesis. One series of mixed oxides of various compositions was prepared from precursors containing basic nickel carbonate and zinc nitrate, whereas the precursors of the other series consist of basic zinc carbonate and nickel nitrate. In both cases, the influence of pre-irradiation with γ rays and accelerated electrons on the properties and hydrogen reduction kinetics of the final mixed oxides were also examined.

EXPERIMENTAL

Two series of mixed oxides with various contents of both components in the range 0–100% were prepared by thermal decomposition of the precursors for 3 h at 480 °C in air. The starting solution of AR grade $Ni(NO_3)_2 \cdot 6H_2O$ was precipitated during intensive agitation with a 15% stoichiometric excess of aqueous K_2CO_3 solution. A carefully washed and dried precipitate of basic nickel carbonate was mixed with $Zn(NO_3)_2 \cdot 6H_2O$ solution in the required ratios of both metals; the suspensions formed were evaporated to dryness at 100 ° C. The concentration of all solutions used was 1 mol l^{-1}. Before the thermal decomposition the precursors (series N) were homogenized by grinding in an agate mortar. An analogous procedure was used for the preparation of the second series (denoted series Z) in which the components were generated in the inverse manner: the precipitates of basic zinc carbonate were mixed with nickel nitrate solution. The optimum conditions of decomposition were first established by DTA measurement of selected precursors differing in composition.

The content of both metals in the mixed oxides was determined by atomic absorption (AA) spectroscopy. The microstructure of the samples was investigated by X-ray diffraction using a TUR M 62 generator with a goniometer. Nickel-filtered Cu Kα-radiation was used ($\lambda = 0.15418$ nm). Specific surface areas were measured by low temperature selective adsorption of nitrogen from an N_2H_2 mixture and the amount of chemisorbed oxygen was determined iodometrically. The standard DTA measurement was performed on a Netzsch STA 409 thermoanalyser within the range 20–600 ° C at a heating rate of 10 ° C min^{-1}.

A portion of each sample prepared was irradiated with ^{60}Co γ rays in air at room temperature to total doses of 328 kGy and 3.7 MGy. Another portion of the samples was further irradiated to a dose of 500 kGy by accelerated electrons of average energy 4 MeV from a high frequency linear accelerator. The reduction kinetics were studied by isothermal thermogravimetry in the range 260–500 ° C using identical conditions for all the initial and radiation-modified mixed oxides. The reduction took place in hydrogen flowing at 56 ml min^{-1} using a 50 mg sample.

RESULTS AND DISCUSSION

Physicochemical properties of mixed nickel and zinc oxides

The chemical analyses (Table 1) show that thermal decomposition of series N, in which amorphous basic nickel carbonate is the major component of the precursor, leads to the formation of super-stoichiometric nickel oxide, whereas in series Z, the sum of the oxides of stoichiometry NiO and ZnO remains unchanged at around 100 wt.% over the whole range of composition. In series N, the presence of higher nickel oxides of variable composition in the range from $NiO_{1.33}$ to $NiO_{1.50}$ has also been demonstrated by thermoanalysis of some samples of different composition. With increasing temperature of the treatment, continuous loss of water and active oxygen takes place and the system converts from the bunsenite phase ($NiO_{1.32}$–$NiO_{1.002}$) to stoichiometric nickel oxide.

The higher levels of super-stoichiometric oxygen in series N compared with series Z (Table 2), and the changes in this parameter induced by pre-irradiation are in accordance with the given characterization. In contrast with series Z, the irradiation of mixed oxides of series N results, in all cases, in a pronounced increase in the amount of super-stoichiometric oxygen, in proportion to the dose of γ rays applied. The zero concentration of this oxygen found with samples containing the highest excess of ZnO, including pure zinc oxide, (samples 18N and 17Z) is a result of the defective structure which determines its n-semiconductive properties [6]. Owing to the presence of air oxygen during the irradiation of the samples, the increase in concentration of super-stoichiometric oxygen can be attributed not only to the shift of equilibrium between various forms of sorbed oxygen in favour of the strongly bound ionogenic form, but also to the subsequent chemisorption of oxygen from the atmosphere onto the new centres generated by ionization. With the samples of series Z containing nickel oxide of nitrate origin, a low starting concentration of adsorption centres, and therefore of chemisorbed strongly bound oxygen on the surface, corresponds to the state of saturation. The changes in concentration are caused by the shift in equilibrium only, regardless on the dose absorbed. The same effect probably leads to the changes in the content of chemisorbed oxygen induced by thermal treatment of samples in various atmospheres for 1 h at 440 °C. Before the oxygen determination, the samples were cooled in the same atmosphere to ambient temperature. As can be seen in Table 3, in series N only, the treatment of pure nickel oxide or mixed oxides leads to an increase in the ionogenic oxygen content; this is more pronounced with the samples treated in an inert atmosphere. In contrast, with the samples of series Z containing a comparable amount of NiO, the influence of the treatment atmosphere is negligible and the concentration of ionogenic forms of oxygen decreases after treatment under the same conditions.

TABLE 1

Notation, composition and specific surface areas (S) of the mixed oxides of series N and Z

Sample	NiO (wt.%)	ZnO (wt.%)	NiO+ZnO (wt.%)	S_N ($m^2\ g^{-1}$)	Sample	NiO (wt.%)	ZnO (wt.%)	NiO+ZnO (wt.%)	S_Z ($m^2\ g^{-1}$)
1N	89.97	0.00	89.97	12.2	1Z	99.00	0.00	99.00	3.6
2N	89.08	2.24	91.32	2.5	2Z	97.37	1.99	99.36	3.9
3N	88.06	3.61	91.67	5.9	3Z	96.23	2.89	99.12	5.3
4N	87.17	5.15	92.32	4.9	4Z	90.54	7.79	98.33	2.4
5N	74.82	14.19	89.01	5.6	5Z	88.70	10.70	99.40	2.7
6N	65.92	24.89	90.81	4.1	6Z	74.47	24.55	99.02	2.4
7N	63.76	25.89	89.65	0.9	7Z	65.84	33.36	99.20	2.3
8N	59.05	29.87	88.92	0.8	8Z	52.14	47.22	99.36	2.1
9N	50.78	42.82	93.60	1.1	9Z	43.18	56.01	99.19	2.5
10N	34.40	63.85	98.20	0.7	10Z	35.52	64.35	99.87	2.1
11N	30.82	69.13	99.95	0.9	11Z	27.12	72.44	99.56	2.8
12N	28.63	70.33	98.96	0.9	12Z	16.16	83.64	99.80	3.4
13N	21.87	76.05	97.92	0.7	13Z	8.04	91.86	99.90	3.9
14N	11.82	86.13	97.95	0.6	14Z	5.09	94.59	99.68	6.5
15N	7.74	91.11	98.85	0.7	15Z	3.80	96.00	99.80	4.3
16N	3.14	96.63	99.77	0.1	16Z	2.46	97.43	00.89	5.4
17N	1.18	98.19	99.37	0.05	17Z	0.00	99.70	99.70	12.7
18N	0.00	99.67	99.67	0.04	–	–	–	–	–

TABLE 2

Content of ionogenic surface oxygen (wt.%) of original (X), pre-irradiated (X_1) and 4-months-stored (X_2) samples of series N and Z

Sample	$X(\times 10^{-3})$	$X_2(\times 10^{-3})$	$X_1(\times 10^{-3})$ Gamma ($D = 3.7$ MGy)	$X_1(\times 10^{-3})$ Gamma ($D = 328$ kGy)	$X_1(\times 10^{-3})$ Electrons ($D = 500$ kGy)
1Z	25.8	12.6	19.1	19.1	12.8
1N	83.4	58.0	714.0	153.0	276.0
2Z	13.0	9.7	16.1	16.1	19.3
2N	50.7	25.0	709.7	185.0	277.0
3Z	9.5	6.4	9.6	25.6	22.4
3N	90.6	45.0	707.1	224.0	333.0
4Z	64.0	34.9	34.9	25.4	35.5
4N	68.1	62.0	794.2	289.0	342.0
5Z	22.1	12.8	9.7	16.2	19.2
5N	112.3	76.0	727.2	261.0	300.0
6Z	19.3	9.6	6.4	9.6	9.5
6N	58.2	39.1	243.1	105.8	218.3
7Z	13.0	6.3	6.2	9.3	9.5
7N	31.1	22.9	227.9	102.1	153.4
8Z	9.6	3.2	3.2	3.2	6.4
8N	30.3	22.0	322.8	147.0	179.2
9Z	7.6	3.2	3.2	1.6	3.2
9N	30.2	32.0	244.0	115.6	147.0
10Z	6.4	3.2	1.6	1.6	1.6
10N	9.6	6.4	201.9	32.1	51.7
11Z	6.4	3.2	1.6	1.6	1.6
11N	6.2	6.5	118.7	32.0	45.0
12Z	6.4	3.2	0.0	0.0	0.0
12N	6.5	6.4	57.2	16.3	15.8
13Z	6.4	0.0	0.0	0.0	0.0
13N	3.2	3.2	50.7	9.6	19.3
14Z	3.2	0.0	0.0	0.0	0.0
14N	3.2	3.2	38.2	6.4	16.1
15Z	0.0	0.0	0.0	0.0	0.0
15N	3.0	0.0	29.0	6.4	12.8
16Z	0.0	0.0	0.0	0.0	0.0
16N	0.0	0.0	32.0	3.2	3.2
17Z	0.0	0.0	0.0	0.0	0.0
17N	0.0	0.0	6.3	0.0	0.0
18Z	–	–	–	–	–
18N	0.0	0.0	0.0	0.0	0.0

Table 2 also shows that the dynamic equilibrium between surface and aerial oxygen, or among the various forms of adsorbed oxygen, changes with time during storage of the samples. The non-monotonic and different dependences of the content of ionogenic oxygen normalized to unit surface area of the samples on composition (Fig. 1) provide a comparison of the

TABLE 3

Influence of thermal treatment for 1 h at 440 °C in various atmospheres on the content of ionogenic oxygen normalized to unit surface area of the samples (Y)

Sample	$Y(g(O^{2-})m^{-2}) \times 10^{-5}$		
	Untreated	Treated in O_2	Treated in N_2
1N	4.7	7.6	20.9
4N	12.5	23.6	57.6
1Z	3.5	2.6	2.6
5Z	4.7	2.3	2.4

different mutual interactions of the components in both series. From the presence of maxima of given dependence in the region of an excess of nickel oxide and in the middle of series N, it can be assumed that the dissociative chemisorption of molecular oxygen takes place not only on the nickel oxide but also on the mixed centres formed by the lower valency ions of both metals. At room temperature in pure zinc oxide only, defects formed by interstitial Zn^+ ions or by oxygen vacancies are present. In addition to the predominant Ni^{2+}–Ni^{2+} adsorption centres, some of the Zn^+ ions present in smaller amounts, can form mixed centres with Ni^{2+} ions so that in some composition regions the oxygen chemisorption is enhanced: $Ni^{2+}\text{–}Zn^+ + O_2 \rightarrow Ni^{3+}\text{–}Zn^{2+} + O^{2-}$.

The mutual interaction of components in both systems is further evident from the magnitudes of specific surface areas and their non-additivity, and from the dependences of this parameter on composition (Table 1). The higher surface areas of the samples at the beginning of series N and at the

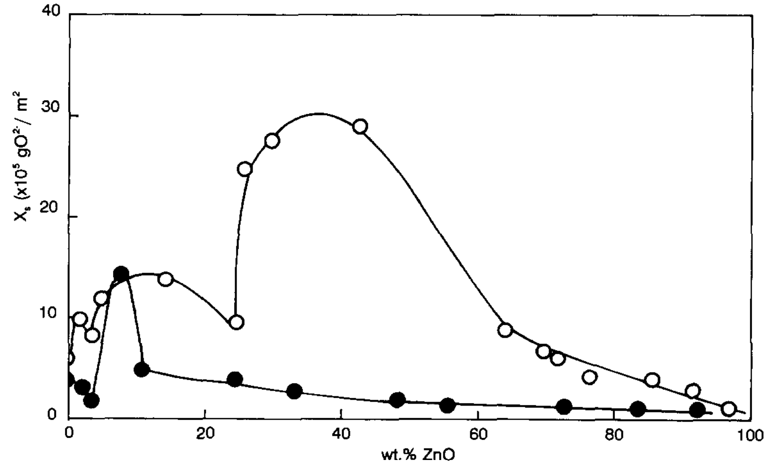

Fig. 1. Dependence of the content of ionogenic oxygen normalized to unit surface area X_s on the composition: ○, series N; ●, series Z.

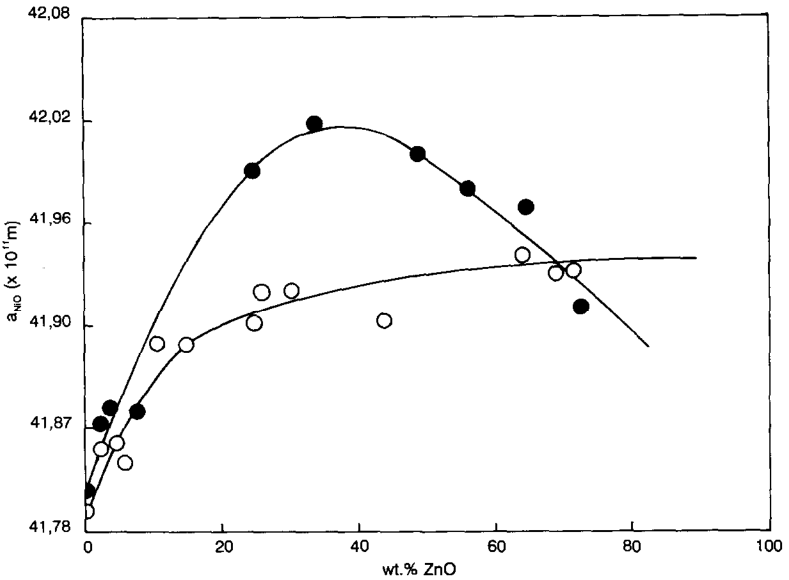

Fig. 2. Dependence of lattice parameter of NiO (a_{NiO}) on the composition: ○, series N; ●, series Z.

end of series Z can be correlated with the surface areas of the corresponding major precursors in these regions of composition, i.e. the amorphous basic carbonates. Their decomposition leads, in all cases, to the formation of finely dispersed oxides of different morphology with higher surface areas than the analogous oxides of nitrate origin.

With the earlier studied series of pure nitrate [3] or carbonate [4] origin, it was found that the lattice parameter of the cubic NiO (a_{NiO} increases with increasing ZnO content in the sample up to approximately 30 mol.% ZnO [7]. This demonstrates that a solid solution of both oxides is produced in this region of composition. Figure 2 shows that the different interaction and distribution of Ni^{2+} ions in the solid with Zn^{2+} ions in solution, and vice versa, during the preparation of mixed precursors are manifested by the different courses of the dependence of a_{NiO} on composition. For the samples of series N the regular increase in a_{NiO} is characteristic over the whole range of composition, whereas in series Z a_{NiO} reaches a maximum at about 35 wt.% ZnO but decreases with further increase in ZnO. Consequently, in both series of mixed genesis the changes in a_{NiO} are not complete when formation of a separate hexagonal ZnO phase takes place. In the samples of series Z, with a higher stoichiometry of NiO or a lower content of ionogenic oxygen, the increase in the lattice parameter of NiO (0.63%) was found to be greater than that in series N (0.39%). Thus one can presume that the effect of "lengthening" of the nickel oxide lattice is caused predominantly by incorporation of ZnO, whereas the contribution of oxygen dissolved in the NiO lattice is negligible. Analogously, as with the pure nitrate or carbonate series, the lattice parameter of metallic nickel (a_{Ni}) increases with increasing ZnO content, and the formation of a new cubic structure of Ni–Zn alloy was observed with the reduced samples of series N and Z: its characteristic reflections appear in series N at ZnO levels as low as about 3.6 wt.%; in series Z, in contrast, its presence was detected at high levels of ZnO only. These findings indicate that ZnO is only partially reduced in mixed systems under conditions when pure zinc oxide is not reduced. The 0.24% increase in a_{Ni} for series N and the 1.60% increase for series Z, are the result of the incorporation of both non-reduced ZnO and a new alloy phase into the nickel lattice.

The positive effect of zinc oxide on the degree of oxidation of nickel by aerial oxygen with primarily reduced original samples is also in accordance with the earlier results [3,4]. In comparison with pure nickel oxide the degree of oxidation of reduced mixed oxides generally increases with increasing ZnO content and reaches various values with respect to the original oxide, depending on the temperature of oxidation. This enhanced affinity of nickel towards oxygen can be attributed to the decrease in the size of nickel microcrystallites as the ZnO content increases, as was proved by X-ray diffraction for both the pure nitrate and carbonate series [7]. The magnitude of the lattice parameter a_{NiO} of mixed re-oxidized samples is lower than in the original samples, but the increase in a_{NiO} with increasing ZnO content remains unchanged. The maximum increase in a_{NiO} in series N is about 0.38%, which is comparable with that of the original oxides, whereas in series Z it amounts to only 0.29% (up to 500 °C) independent of the temperatures of the primary reduction and oxidation.

Kinetics of hydrogen reduction and the influence of pre-irradiation

A higher reactivity of the mixed oxides with the major reducible component (NiO) or carbonate origin (series N) manifests itself by relatively high reduction rates in the temperature region 290–440 °C up to sample 15N, whereas in series Z, only the first three samples with the highest excess of NiO are reduced at a measurable rate at 350 °C, and at 500 °C the reduction proceeds up to sample 16Z. Maximum weight losses (degrees of reduction) were compared with the theoretical values calculated assuming that nickel oxide is the only reducible component of the system. Figure 3 shows that the degree of reduction over the theoretical value, corresponding to the total reduction of NiO, increases monotonically with increasing ZnO up to the maximum at 80 wt.% ZnO in series Z only. With the earlier studied series of mixed oxides of pure carbonate or nitrate origin, the dependences show exactly the same course as series Z, including the position of the maximum. However, the excess of reduction reaches only 15% for the carbonate series and does not exceed 5% with the samples of the nitrate series [4]. In contrast with the series Z, the relatively high degree of "over-reduction" already

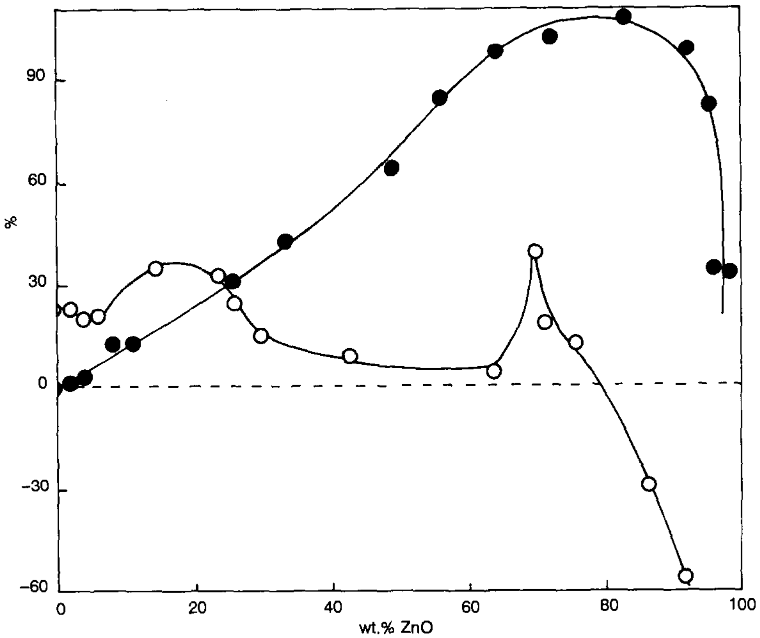

Fig. 3. Dependence of the percentage reduction over the theoretical value (corresponding to the total reduction of NiO) on the composition: ○, series N; ●, series Z.

present in the initial samples of series N demonstrates the presence of a strongly super-stoichiometric nickel oxide. From X-ray analysis of the samples reduced at higher temperatures, it has been determined that the partial reduction of ZnO takes place in both series and a new metallic alloy phase is formed. Reduction of zinc oxide contributes to the theoretical weight loss even in samples containing a low amount of ZnO in series N, whereas in series Z this is the major effect and the degree of reduction of ZnO increases with its increasing content in the samples up to the maximum.

As with the series of mixed oxides of pure carbonate or nitrate origin [4], the rate of reduction of nickel oxide in series N and Z is mostly affected by the second component in the region of a homogeneous solid solution, i.e. up to 25–30 wt.% ZnO. As can be seen from Fig. 4, the interaction of zinc oxide with stoichiometric nickel oxide (series Z) shows a different dependence of the rate of reduction on composition compared with the same system containing a non-stoichiometric nickel oxide (series N). In the former case, the rate of reduction decreases monotonically with ZnO content, from 5 wt.% ZnO, as a result of the superposition of two negative effects which retard the reduction of nickel oxide. In the region of small admixtures of ZnO, the mixed adsorption centres are exploited and an increase in the surface concentration of ionogenic oxygen takes place. The super-stoichiometry of nickel oxide induced in this manner is formed only by strongly

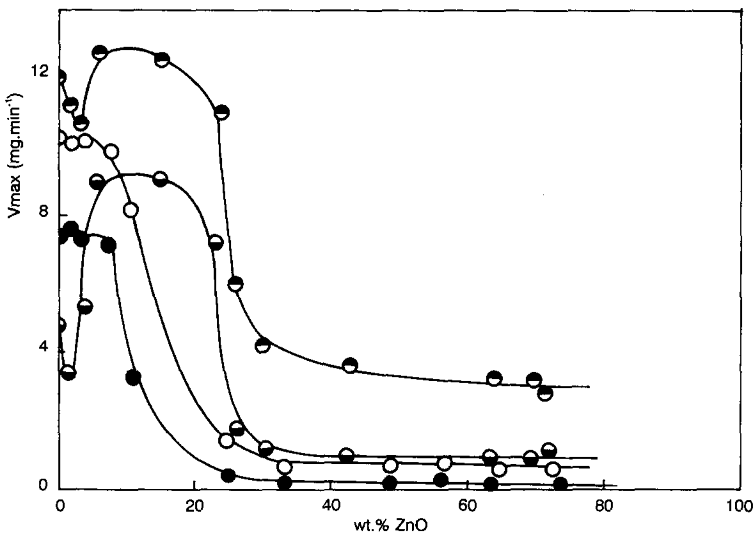

Fig. 4. Plot of maximum reduction rate V_{max} vs. composition: ◓, series N (380 ° C); ◒, series N (290 ° C); ○, series Z (470 ° C); ●, series Z (440 ° C).

bound forms of oxygen and leads to a lowering of the reduction rate]5]. Moreover, the donor chemisorption of hydrogen on the surface of nickel oxide is lowered by the incorporation of ZnO, a thermodynamically more stable, n-semiconductive oxide. Hence, with increasing content of ZnO, the rate of reduction rapidly decreases. The sigmoidal shape of the reduction curves of these samples shows that the nucleation is a rate-determining step. Above 25 wt.%, ZnO forms a separate phase and has practically no influence on the rate of reduction of nickel oxide; a slight decrease in the reduction rate at lower temperatures can be attributed to the mechanical blocking of the reaction interface by accumulating ZnO.

At the beginning of series N the increase in the levels of ionogenic oxygen, caused by the small amount of ZnO, is also associated with a decrease in the rate of reduction (Fig. 4). Further additions of oxygen-deficient zinc oxide, however, exhaust the strongly bound super-stoichiometric oxygen of NiO, compensating simultaneously its super-stoichiometry [4,8] according to the equation $Ni^{3+} + Zn^{+} \rightarrow Ni^{2+} + Zn^{2+}$. On the surface adsorption centres of nickel oxide, i.e. on the weakly bound oxygen (neutral form), reduction begins with a rapid sorption of hydrogen. A high concentration of nuclei of the product is formed by the subsequent surface reduction. The kinetic curves for the reduction of these samples show, in contrast with series Z, a shift in the maximum reduction rate towards the beginning of the processes, owing to the rapid formation of a continuous reaction zone on the surface or in the near sub-surface grain layers. Under these conditions, the metallic phase of nickel induces the reduction of the second components zinc oxide; this has been confirmed by X-ray analysis.

In this local region of composition the addition of ZnO leads to an increase in the rate of reduction. The higher reactivity of the samples of series N in which nickel oxide is the major component, including pure NiO, as well as the higher concentration of adsorption centres for all forms of oxygen, compared with samples of the same composition in series Z, is probably connected with the dispersion of the nickel oxide. The results of X-ray diffraction show that the average size of NiO microcrystallites in series Z, up to 10 wt.% ZnO, is 7–10 nm; this slowly decreases with increasing ZnO content. In the same region of composition of series N, the NiO microcrystallite size is only 3 nm and this rapidly increases with increasing ZnO content. In both series, the maximum changes in the rate of reduction of nickel oxide caused by the addition of the second component, in the region up to 25 wt.% ZnO, are connected with an increase in the apparent activation energy: from 55 for pure NiO to 130 kJ mol^{-1} in the temperature interval 260–320 °C for series N and in the interval 350–470 °C for series Z. A low average value of this quantity, 30 ± 5 kJ mol^{-1}, in the region of high temperature reduction of series N (370–440 °C) is the result of internal transport processes.

In both series, the behaviour of the oxides following thermal treatment under the conditions given above, results in different reactivities. In series N it leads to the activation of the surface by the removal of bound water and the desorption of gas impurities. In addition to the increase in ionogenic forms of oxygen (Table 3), the adsorption of weakly bound, easily reducible oxygen increases. The rate of reduction therefore increases steeply, being 2.5 times higher than for the original samples. In series Z, containing stoichiometric nickel oxide with a small surface-adsorption capacity, the content of chemisorbed oxygen is slightly lowered and the rate of reduction of both pure nickel oxide and mixed oxides remains practically unchanged.

The effect of pre-irradiation on the reduction kinetics of mixed oxides is demonstrated in Fig. 5 by the dependence of the quantity $\Delta V_{\max}$ on composition

$$\Delta V_{\max}\ (\%) = 100(V^{+}_{\max} - V_{\max})/V_{\max}$$

where $V^{+}_{\max}$ is the maximum reduction rate of irradiated samples and $V_{\max}$ is the same quantity for the non-irradiated original samples. As can be seen, pre-irradiation results in a negative effect (a decrease in the reduction rate) in the region of excess nickel oxide in series N. With increasing content of the second component, an inversion of this effect takes place and in the region over 25 wt.% ZnO, the irradiated samples are reduced at a higher rate than the original mixed oxides. The negative radiation effect reaches a maximum with higher doses of γ rays whereas the maximum positive effect is induced by accelerated electrons. The decrease in the reduction rate of samples containing an excess of nickel oxide can be attributed to the increase in the concentration of strongly bound ionogenic oxygen. Reduc-

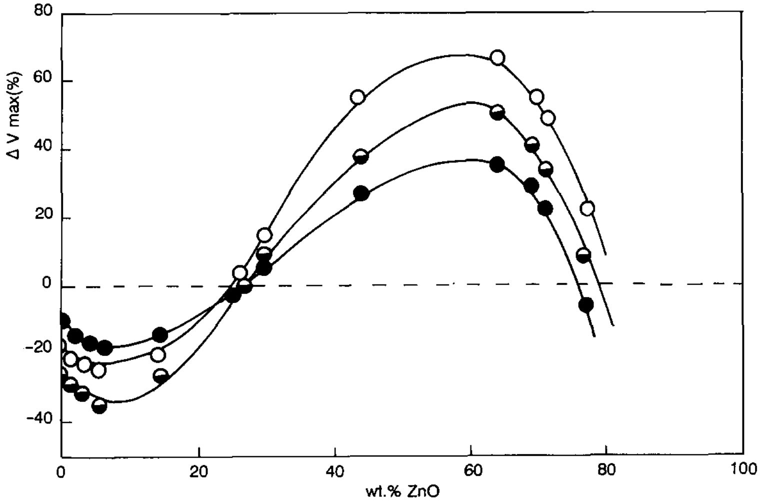

Fig. 5. Effect of the pre-irradiation on the maximum reduction rate of the samples (series N) of various compositions: ○, electrons ($D = 500$ kGy); ⊖, γ rays ($D = 3.7$ MGy); ●, γ rays ($D = 328$ kGy).

tion of non-stoichiometric nickel oxide, the super-stoichiometry of which is caused only by this form of oxygen as a result of irradiation, is controlled by the slow donor chemisorption of hydrogen and proceeds at a lower rate in comparison with the unirradiated samples [5,9]. In a two-component system, the negative effect of radiation can be counteracted by the competing positive effect, i.e. by the stabilization of non-equilibrium charge or point defects on the biographic lattice perturbations. The presence of quasi-free electrons increases the reactivity of the interface and the decomposition processes, including reduction, are thus accelerated. The inversion of the radiation effect, which was also observed with another two-component oxide system containing nickel oxide [2], takes place in the region of about 25 wt.% ZnO, where this oxide forms a separate phase. In general, with increasing numbers of boundaries of interacting phases, the concentration of biographic defects, as well as the probability of capture and stabilization of radiation-induced defects, increases.

A maximum absolute value of the negative effect for a higher dose of γ radiation is in accordance with the maximum increase in ionogenic oxygen content. Considering that the reduction proceeds at a maximum rate in near sub-surface grain layers, accelerated electrons, in contrast with γ radiation, will also deposit a higher portion of their energy in these layers, influencing $V_{\max}$ to a greater extent; thus a higher value of the positive effect following irradiation by electrons can be assumed, as seen in the experimental results. The changes in the content of ionogenic oxygen after irradiation of samples in series Z containing stoichiometric nickel oxide are negligible (Table 2), so that there is practically no negative effect. The prevailing positive effect of irradiation, which was also observed with other systems containing stoichiometric nickel oxide [10], cannot be quantified because of the relatively high temperature necessary for the measurable reduction of the greater part of the samples. At the temperature used (440 °C), recovering and recombination processes take place to a great extent, so that the irradiation effects disappear. The quantity V_{max} changes in the range ±15%, which is close to the upper limit of the total error of measurement.

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