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PHYSICO-CHEMICAL PROPERTIES AND HYDROGEN REDUCTION REACTIVITY OF NICKEL AND COBALT MIXED OXIDES OF VARIOUS STOICHIOMETRY

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Investigations have been made of the effects of the origin and some physico-chemical parameters on the kinetics of reduction with hydrogen of two series of mixed nickel and cobalt oxides differing in the stoichiometry of the two oxides. The first series, consisting of non-stoichiometric mixed oxides NiO-Co_3O_4 of various compositions, were prepared by calcining the mass of coprecipitated hydroxides in air. High-temperature treatment of the oxides obtained led to the second series, which consisted of stoichiometric NiO and non-stoichiometric CoO. The reactivity of the mixed oxides towards reduction with hydrogen varied with the phase composition and with the amount and ratio of various forms of super-stoichiometric oxygen in the systems under study.

In the group of 3d transition metal oxides, great attention has been paid to the systematic study of Co_3O_4 with the spinel structure from various aspects. Depending on the conditions of preparation, i.e. the temperature and atmosphere of the decomposition of the starting cobalt(II) salts, variations are observed in the composition and oxygen distribution in excess of the stoichiometric amount [1, 2], and in the magnetic [3], crystallographic [4] and other physico-chemical properties of Co_3O_4. Pronounced differences in textural and structural characteristics, which are correlated with different catalytic activities, have been observed for samples of Co_3O_4 prepared either by thermal decomposition of the hydroxide $Co(OH)_2$ and oxyhydroxide CoOOH, or by their mechanochemical transformation (grinding procedures [5]). The Co_3O_4 used as catalyst in some oxidation process, changes not only its composition during the reaction, but also the mechanism of the reaction [6].

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In contrast with the catalytic activity, the effect of the prehistory of transition metal oxides on their chemical reactivity in various reactions has so far been insufficiently studied. The aim of the present study was to investigate some physico-chemical parameters of nickel and cobalt mixed oxides with various stoichiometries. The hydrogen reduction of these oxides was used as a test of their reactivities.

Experimental

The basic series of mixed oxides with different compositions in the range 0-100% of each component were prepared by thermal decomposition of coprecipitated hydroxides for 4 h at 400° in air. Starting aqueous 1 $mol.l^{-1}$ solutions of AR grade $Ni(NO_3)_2.6H_2O$ and $Co(NO_3)_2.6H_2O$ were mixed together in the required ratios and then precipitated during intensive agitation with a 10% stoichiometric excess of a 3 $mol.l^{-1}$ solution of KOH. Carefully washed and dried products were calcined and pulverized. The conditions of decomposition were established previously by DTA measurement of selected samples of precursors (mixed hydroxides) differing in their composition.

The contents of both metals in the mixed oxides were determined by AA spectroscopy. The microstructures of the samples were investigated by X-ray diffraction on a Dron-3 apparatus using CrK_α radiation. Specific surfaces were measured by low-temperature selective adsorption of nitrogen from a N_2/H_2 mixture, and the morphology of mixed oxides was studied by using a JSM-50A (Jeol) scanning electron microscope. The content of chemisorbed oxygen was determined in part by the classical iodometric method in strongly acidic solution [7], and in part by the KI (pHx) method, determining the distribution of the oxidation power of the surface excess oxygen [8].

The standard DTA measurement was performed on the Netzsch STA 409 thermoanalyser within the range 20-1000° at a heating rate of a 10 deg min^{-1}. The reduction kinetics was studied by isothermal thermogravimetry in the temperature range 290-420° at a hydrogen flow rate of 56 ml min^{-1}, using a 50 mg weight of sample. Under these conditions, the reduction kinetics of the samples at an arbitrary composition is independent of the flow rate of the reduction gas.

Results and discussion

Physico-chemical properties of nickel and cobalt mixed oxides

It follows from the results of X-ray analysis (Table 1) that, under the conditions of thermal decomposition used, nickel oxide and Co_3O_4 with the spinel structure are formed as the major components of the system studied. Increases in the lattice parameter and the size of the coherent regions of nickel oxide with increasing content of cobalt up to sample No 4 indicate that, in the region of a high excess of NiO, a substitution solid solution of both oxides is produced, the cubic NiO structure being maintained. In the middle of the series (samples 5-10), the size of the coherent regions of the separate phase of NiO decreases with further increasing content of Co_3O_4. A similar influence of both oxides can be observed in the second edge of the series (excess of Co_3O_4), where the lattice parameter of Co_3O_4 increases with increasing nickel oxide amount (samples 15-10). With regard to the results of chemical analysis (Table 2) and the experimentally found value of the lattice parameter of pure Co_3O_4 (sample No 15), which is lower (D = 0.8078 nm) than the tabulated one (D = 0.8084 nm), the presence of small amounts of lower-valency cobalt oxides, and especially of CoO, in this region of composition can not be discounted.

As concerns the mechanism of Co_3O_4 formation, this oxide is formed during the thermal decomposition of the precursor in air directly, without the intermediate stage of metallic Co formation and subsequent oxidation. The DTA curves of the precursors (mixed hydroxides) of various compositions in all cases show two endothermic effects (Fig. 1). The first, very broad effect lies in the range 50-200° and the second, sharp one, whose magnitude decreases with increasing content of cobalt, reaches a maximum at about 300°. From the experimental weight losses for the two stages of decomposition, it can be deduced that the dried precursor with prevailing content of cobalt consists of the oxyhydroxide CoOOH rather than pure $Co(OH)_2$, together with residual water over the composition of CoOOH ($=Co_2O_3.H_2O$). After the release of water at a low temperature, the dehydration of molecular water continues simultaneously with the loss of oxygen and the transformation $CoHO_2 \rightarrow Co_3O_4$, the theoretical weight loss for this stage being 12.7%.

Table 1 Phase composition, size of coherent regions (L) and lattice parameters (D) of NiO-Co_3O_4 mixed oxides (basic series)

Sample	Phase analysis	L (.0.1 nm) in the line ⊥ to (hkl)	L (.0.1 nm) MO average	L (.0.1 nm) M_3O_4 (hkl)	D (.0.1nm) ±0.001 MO	D (.0.1nm) ±0.001 M_3O_4
1	only NiO	(111) 457				
		(200) 439	472	-	4.178	-
		(220) 519				
2	only NiO	(200) 517	530	-	4.180	-
		(220) 543				
3	only NiO	(200) 597				
		(220) 608	602	-		
4	only NiO	(200) 802				
		(220) 753	777	-	4.181	-
5	strongly NiO	(200) 492				
	indication Co_3O_4	(220) 419	455	immeasurable		
6	strongly NiO	(200) 405				
	slightly Co_3O_4	(220) 404	405	(220) 421		
7	strongly NiO	(200) 360				
	middle strongly Co_3O_4	(220) 353	356	(220) 416		
8	middle NiO	(200) 275				
	middle Co_3O_4	(220) 277	276	(220) 415		
9	middle Co_3O_4	(200) 236				
	slightly NiO		236	(220) 405		
10	strongly Co_3O_4	(200) 229	229	(220) 416	-	8.095
	slightly NiO					
11	strongly Co_3O_4	immeasurable	-	(220) 484	-	
	very slightly NiO					
12	strongly Co_3O_4	-	-	(220) 521	-	
13	only Co_3O_4	-	-	(220) 468	-	8.083
14	only Co_3O_4	-	-	(220) 530	-	
15	only Co_3O_4	-	-	(220) 649	-	8.078

The fact that the mechanism of formation of Co_3O_4 does not involve intermediates and their additional oxidation (no weight increments were observed) is in accordance with the conclusions in paper [9], which deals with magnetic measurements during the thermal decomposition of various cobalt(II) salts.

Analogously, the starting precursors with an excess of nickel can be interpreted as solid solutions of hydrated NiO_2 in NiOOH, or as a mixture of the phases NiOOH and $Ni_3O_4.nH_2O$. With continually increasing temperature, the dehydration proceeds, but the loss of oxygen is higher due to the transformation $Ni_3O_4 \rightarrow NiO_{1+x}$, where x represents the superstoichiometric oxygen of nickel oxide.

Table 2 Composition, specific surface areas of NiO-Co_3O_4 mixed oxides (S) and corresponding selected precursors (S_1)

Sample	Wt.%			S	S_1
	NiO	Co_3O_4	$NiO+Co_3O_4$	($m^2.g^{-1}$)	
1	92.20	0.00	92.20	35.2	
2	89.77	2.46	92.23	31.6	
3	88.01	6.69	94.70	26.5	56.5
4	85.40	9.61	95.01	17.7	
5	80.30	19.23	99.53	23.7	
6	70.28	28.98	99.26	26.1	
7	61.51	38.46	99.97	25.2	
8	49.98	47.30	97.28	26.7	46.3
9	41.28	58.57	99.85	20.1	
10	28.87	70.04	98.91	12.8	
11	19.32	78.78	98.10	15.2	
12	12.19	87.76	99.95	23.5	
13	7.94	92.00	99.94	22.8	42.2
14	3.70	95.92	99.22	22.5	
15	0.00	99.11	99.11	18.5	

Figure 2 demonstrates the dependence of the content of iodometrically determined superstoichiometric oxygen, normalized to unit surface area, on the composition of the mixed oxides. The analogous dependence obtained by the KI (pH = 7.1) method shows the same character, but the absolute values of the quantities measured are approximately only half the previous ones. This fact proves that in the former case (acidic solution) the oxidation of I^- ions is not restricted only to the surface excess of oxygen, but also extends to the bulk oxygen owing to the partial solubility of the sample. The significantly non-monotonous course of this dependence, with maxima in both marginal regions of the composition, or with a maximum in the middle of the series, indicates that the dissociative chemisorption of molecular oxygen proceeds predominantly on the centres consisting of the pairs of lower-valency ions of both pure metals (Co^{2+}-Co^{2+}, Ni^{2+}-Ni^{2+}) or by mixed pairs: $Co^{2+}\text{-}Ni^{2+} + O_2 \rightarrow Co^{3+}\text{-}Ni^{3+} + 2O^-$.

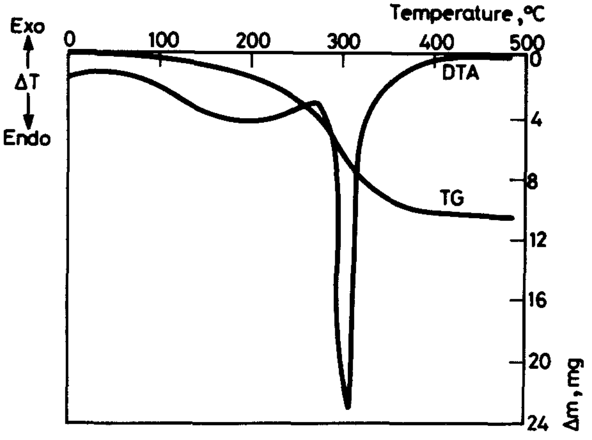

Fig. 1 DTA and TG curves of the precursor (mixed hydroxides) corresponding to the sample No. 3

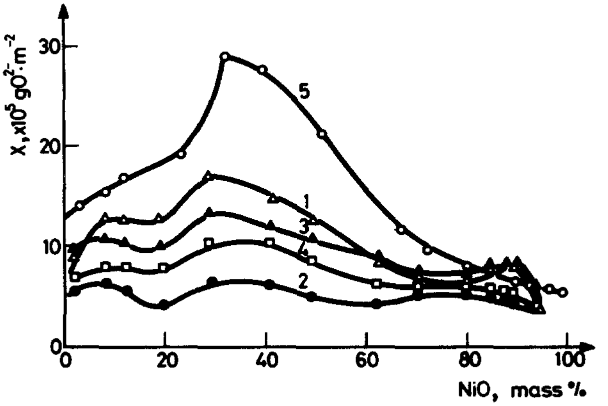

Fig. 2 Content of the superstoichiometric oxygen normalized to unit surface area X (g O^{2-}/m^2) vs. composition basic series 1 - freshly prepared; 2 - after 4 months storage; 3 - after 12 months storage; 4 - after 14 months storage; 5 - calcinated series

The content of superstoichiometric oxygen was measured within 14 months after storage of the samples in contact with the atmosphere. It follows from Fig. 2 that the value of this parameter changes periodically in time without achievement of an equilibrium state. Simultaneously, the character of the dependence given is changed. the ageing of the samples is therefore connected not only with a change in the concentration of adsorption centres, but also with the modification of their structure and configuration.

A high-temperature treatment of the samples of the basic series at 930°, for half an hour in air leads to the equilibrium concentration of the adsorption centres (these series will be designated below as the calcined system). It can be seen from Fig. 2 that the thermal treatment leads to a pronounced increase in the absolute amount of superstoichiometric oxygen invarying in time in the samples containing an excess of cobalt.

Table 3 Composition and specific surface areas (S_2) of the samples of calcinated series

Sample	Wt.%			S_2,
	NiO	CoO	NiO+CoO	$m^2.g^{-1}$
1	99.18	0.00	99.18	2.9
2	96.52	2.34	98.86	2.7
3	-	-	-	-
4	89.78	9.11	98.89	2.3
5	80.13	18.92	99.05	1.5
6	72.89	26.80	99.69	1.9
7	67.31	31.75	99.06	1.4
8	51.82	45.21	97.03	2.1
9	39.49	59.05	98.54	2.2
10	32.13	64.26	96.39	2.0
11	22.73	75.94	98.67	1.8
12	11.43	72.64	84.07	1.5
13	7.36	84.96	92.32	1.8
14	2.41	84.07	86.48	2.1
15	0.00	86.10	86.10	1.8

From the chemical (Table 3) and X-ray analysis, it follows that the calcined system consists of practically stoichiometric nickel oxide (the samples with a high excess of this are greenish-yellow) and cobalt(II) oxide. Up to a content of 50%, both oxides of the system are present as a solid solution. Above this composition boundary, CoO forms a separate, very finely dispersed phase. A small amount of residual, non-transformed Co_3O_4 in the samples containing a high excess of Co was also proved.

The samples of the basic series exhibit different behaviour in the course of additional thermal treatment in air as compared with the calcined system. The initial endoeffect in the DTA curves of the calcined samples corresponds to the desorption of surface-bound water, and the following marked exoeffect, connected with the weight increment (Fig. 3, TG curve) to the oxidation $CoO \rightarrow Co_3O_4$. At temperatures higher than 800°, the Co_3O_4 formed decomposes the magnitude of the characteristic endoeffect being proportional to the amount of this oxide in the system. Thermal treatment of the samples of the basic series under comparable conditions shows a continuous weight loss due to the release of water and later of active oxygen. A sharp endoeffect in the decomposition of Co_3O_4 is detectable beginning with sample No. 7. With increasing content of nickel oxide, the position of this endoeffect shifts towards lower temperatures. The ageing of the samples of the basic series is reflected in the thermoanalytical curves by the 5-10 times higher amount of water absorbed in comparison with the freshly prepared mixed oxides, and by the above-mentioned changes in the content of superstoichiometric oxygen.

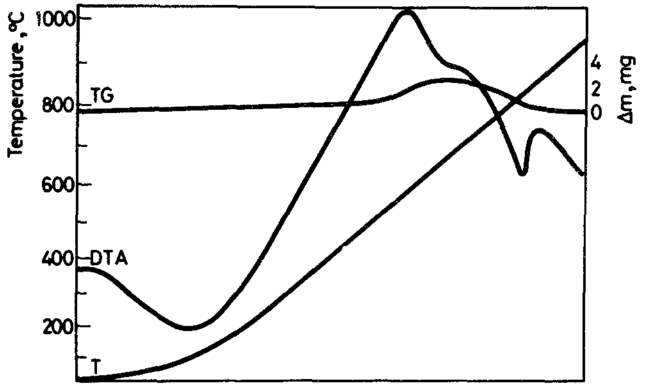

Fig. 3 Thermoanalytical curves of the sample No. 9 of calcinated series

The non-monotonous dependence of the specific surface areas of both series of mixed oxides (Tables 2 and 3) on the composition also indicates the higher degree of mutual interaction (epitaxial contact) of the two components as compared with their mechanical mixture. Similarly as with the starting precursors, the surface areas generally increase with increasing content of nickel oxide. However, their absolute values decrease owing to the sintering processes in the genetic sequence: precursor - basic series - calcined series of mixed oxides. In contrast with the mixed systems prepared by the thermal decomposition of various crystalline salts (chlorides, nitrates, etc.), the same samples obtained by the decomposition of rather amorphous precipitates (carbonates, hydroxides) consist of grains and their agglomerates with a rough surface (Fig. 4).

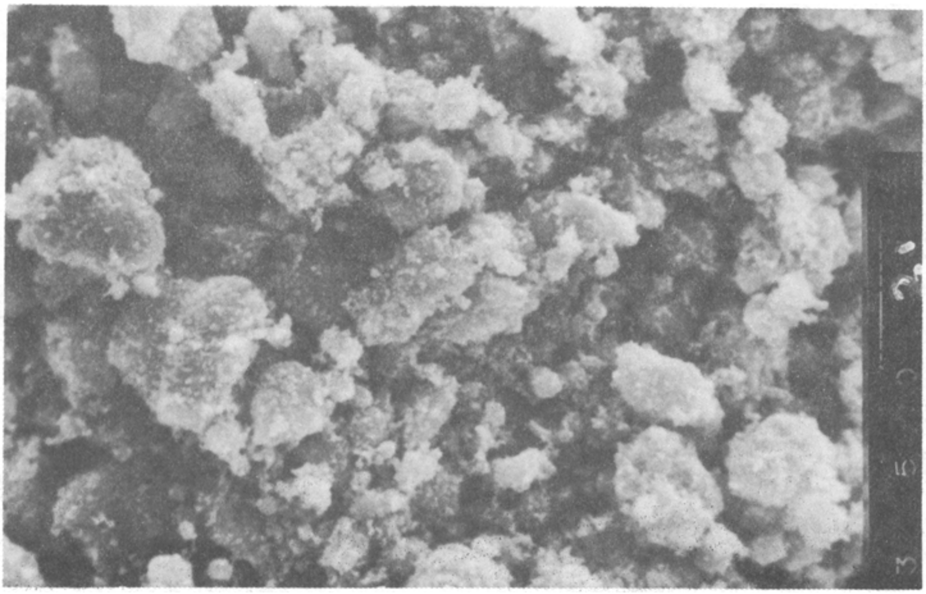

Fig. 4 Electron micrograph of sample No. 12 (basic series) Magnification 10^3x. The line segment indicated corresponds to 20 μm

Kinetics of hydrogen reduction

Figure 5 illustrates the courses of reduction of samples of various compositions at different temperatures. It can be seen that the reduction of mixed oxides with a prevailing content of cobalt proceeds as a two stage reaction, corresponding to the partial steps $Co_3O_4 \rightarrow CoO$ and $Co(Ni)O \rightarrow Co(Ni)$. The two consecutive reactions can not be distinguished at a higher reduction temperature (curve 1) or for samples containing an excess of NiO (curve 2), where the reduction curve displays a sigmoidal shape typical of that for pure nickel oxide. Analogously, the two-stage course of the reduction was not observed for the calcined series or for the previously studied system of nickel and cobalt mixed oxides obtained by thermal decomposition of coprecipitated basic carbonates in a dry nitrogen atmosphere [2]. In this latter case, additionally to the majority components NiO an Co_3O_4, the system contained further separate phases of cobalt(II) oxide and a new structure of a compound denoted by $Co_{3-x}Ni_xO_4$ [10]. An increase in the reduction reactivity of the two cobalt oxide phases of various stoichiometries which are in close contact, is revealed by the steep starting part of the reduction curve and the high initial reduction rate of the mixed oxides with a prevailing content of cobalt [2]. In contrast with this system, an analogous effect was not found either for the basic series or for the calcined samples at present studied.

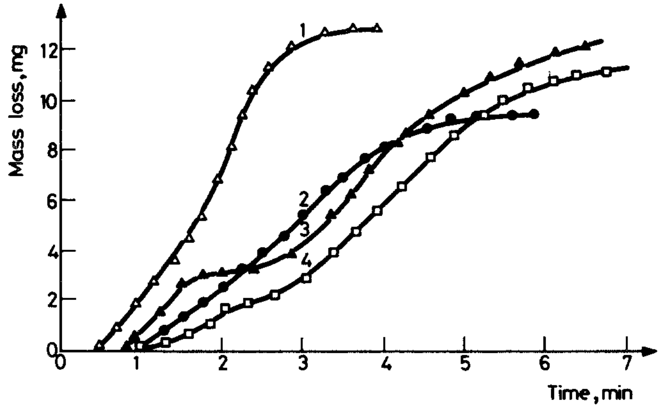

Fig. 5 The courses of reduction of samples No. 3, 8 and 12 of basic series at different temperatures 1 - 12, 390°C; 2 - 3, 330°C; 3 - 12, 330°C; 4 - 8, 330°C

As proved previously [2, 11, 12], the reactivity of non-stoichiometric nickel oxide in the hydrogen reduction depends on the ratio of the neutral, weakly bound and ionogenic, strongly bound forms of its super-stoichiometric oxygen. This ratio can be altered either via the preparation conditions or by thermal and radiation treatment of the final oxide [12]. It follows from Fig. 2 that the content of ionogenic oxygen in the basic series changes markedly during the ageing of the samples; hence, a corresponding change should be expected in their reactivity. Table 4 shows an increase in the rate of the second partial reduction in the whole range of composition for the samples after storage for 4 months. This acceleration, which is especially apparent for the samples containing an excess of cobalt and which was also found for the initial part of the reduction corresponding to the partial reaction $Co_3O_4 \rightarrow CoO$ is in accordance with a decrease in the amount of strongly bound oxygen as compared with the initial state. The change in the reduction rate is expressed by the quantity Δk (%) = 100 $(k^+ - k)/k$, where k^+ is the rate constant of reduction of the samples after storage and k is the value pertaining to the initial, fresh mixed oxides. The rate constants were calculated from the equation corresponding to the shrinking core model, which quantitatively describes the reduction kinetics of nickel and cobalt mixed oxides [2] over a wide range of degree of reduction.

Table 4 Effect of ageing (Δk) and thermal treatment (Δk_1) on the rate of reduction of mixed oxides - basic series

Sample	Δk^a, %	Δk_1^b, %
1	26.9	-24.4
2	38.8	
3	33.3	
4	32.5	-41.6
5	33.4	
6	30.1	
7	50.6	
8	59.4	-54.7
9	81.7	
10	46.7	
11	77.2	
12	42.8	-61.5
13	38.3	
14	38.6	
15	68.7	-65.7

Δk^a, samples measured after 4 months storage, reduction temperature 290°C

Δk_1^b, selected samples were thermally treated for 1 h at 400°C on the air, reduction temperature 360°C

In order to eliminate the influence of absorbed water, selected samples of various compositions were dried for 1 h at different temperatures up to 400°, which lies deeply under the transformation temperature of Co_3O_4 and does not lead to a lowering of the surface areas by sintering. In all cases, an increase in the content of ionogenic oxygen with increasing temperature was proved as a result of enhanced chemisorption on the new surface centres activated by thermal treatment. The effect of the treatment on the reduction kinetics of these samples is shown in Table 4, using the quantity Δk_1 defined analogously to Δk, where k^+ is the rate constant of the reduction of the sample treated at 400°. From the results, the decrease in the rate of reduction of treated samples ($\Delta k_1 < < 0$) is evident in the whole range of composition.

The high-temperature treatment of mixed oxides leading to the calcined series is connected with the transformation of Co_3O_4 to cobalt(II) oxide and with the loss of a weakly-bound, iodometrically non-detectable form of superstoichiometric oxygen in NiO, which is the cause of its high reactivity. Figure 2 reveals that the samples with a prevailing content of the non-stoichiometric cobalt(II) oxide, whose exact composition is $CoO_{1.07}$, have a higher affinity towards oxygen as compared with the initial series. Analogously, an increase in the number of adsorption centres of oxygen after the surface reduction of Co_3O_4 was proved in [13]. In contrast, in the region with prevailing NiO content, the change in the amount of ionogenic oxygen after high-temperature treatment of the samples is substantially lower. This fact is in accordance with the previous finding that the total loss of strongly-bound oxygen from NiO is achieved either at a higher temperature of treatment in the air (over 1000°), or at a lower one (about 800°) in the inert atmosphere [14]. In contrast with the low-temperature activation, the new free adsorption centres can not be of use as they are destroyed by the sintering, so the nickel oxide is converted to the stoichiometric one.

The quantity Δk_2 defined as above and characterizing the effect of high-temperature treatment on the rate of reduction of samples varies only slightly with the composition from 40% (excess of nickel) to 60% (excess of cobalt). Since the specific surface areas of the calcined samples are an order of magnitude lower than those of the original samples (Table 3), the decrease in the rate of reduction of the calcined series can not be attributed only to the lowering of this quantity as a result of high-temperature treatment.

The mutual interaction of the two components in the calcined series is demonstrated in the marked dependence of the rate and degree of the secondary reduction of the reoxidized samples on the composition. In these experiments, the selected samples after primary reduction were oxidized in an air flow up to a constant degree and then reduced again at the same temperature. The primary reduction yields a substitution solid solution of the two metals. In addition to the hexagonal structure, the presence of cobalt with a cubic lattice, probably stabilized at temperatures lower than 480° by reducing hydrogen, was also proved. In the region of a high excess of NiO, the slow partial oxidation proceeds to a low degree, owing to the formation of a compact passivating layer of the oxide on the grain surface. The rate of secondary reduction is lower than that of the primary process and the degree achieved does not correspond to the oxidation degree. With increasing content of cobalt, both the rate and the degree of the oxidation increase and the rate of secondary reduction of nascent cobalt oxides with a non-stabilized structure is 2-3 times higher than that for the primary process.

The influence of the composition on the reduction kinetics of the oxides of the basic series follows from Fig. 6. Since the reduction proceeds at the maximum rate in the surface and near surface grain layers, the reduction

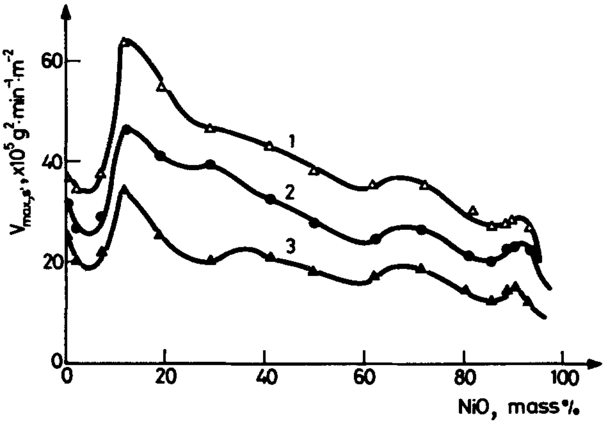

Fig. 6 Dependence of the specific maximum reduction rate $V_{max,S}$ (g^2/m^2.min) of the samples of basic series on composition. Reduction temperature: 1 - 390°C; 2 - 360°C; 3 - 330°C

was characterized by the maximum rate normalized to unit surface area ($V_{max,s}$).

In the region of a high excess of Co_3O_4, where all the minority NiO is bound in the solid solution, its small admixture leads to a lowering of the reduction rate. With further increasing content and the formation of a separate phase of NiO, the reduction is accelerated owing to the enhanced nucleation on the interface, and the dependence of $V_{max,s}$ on the composition shows a significant maximum. In the second marginal region, the reduction of NiO is accelerated by small admixtures of Co_3O_4 up to the composition corresponding to the maximum content of solid solution bounding all the Co_3O_4. The formation of its separate phase is connected with the lowering of the epitaxial contact of the two components and with the slight decrease of the reduction rate. With further increasing content of free Co_3O_4, the rate of the reduction again continuously increases.

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Zusammenfassung — Es wurden Untersuchungen über den Einfluß des Ausgangspunktes und einiger physikalisch-chemischer Parameter auf die Kinetik der Reduktion zweier Reihen von Nickel- und Cobalt- Oxidgemischen mit Wasserstoff angestellt, die sich in der stöchiometrischen Zusammensetzung der beiden Oxide voneinander unterscheiden. Die erste Reihe von nichtstöchiometrischen NiO-Co_3O_4 Oxidgemischen unterschiedlicher Zusammensetzung wurde durch Kalzinieren kogefällter Hydroxide an Luft gefertigt. Das Erhitzen der erhaltenen Oxide auf hohe Temperaturen lieferte die zweite Reihe Oxidgemische, bestehend aus stöchiometrischem NiO und nichtstöchiometrischem CoO. Die Reaktivität der Oxidgemische bei der Reduktion mit Wasserstoff verändert sich mit der Phasenzusammensetzung sowie mit Menge und Verhältnis verschiedener Formen von superstöchiometrischem Sauerstoff in den untersuchten Systemen.