

Effect of Biography on Stoichiometric Composition and Chemisorptive Properties of Nickel Oxide (Oxygen Chemisorption)

J. DEREŃ AND J. STOCH

*Institute of Solid State Chemistry, School of Mines and Metallurgy,
Kraków, Poland*

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One of the main properties of oxide catalysts of NiO type is their excess oxygen content. Various analytical methods employed in determination of this content have some limitations and yield different results. On the basis of the results reported in the literature and of the result obtained in the present work, the reasons for these differences are discussed. Analysis of the experimental results shows that oxygen coverage θ is a function of annealing temperature showing a maximum in the range 700–900°C. Full elucidation of such a course of changes is not possible at present owing to the scarcity of experimental data. The hypothesis is put forward which relates the course of the $\theta = f(T_{\text{anneal}})$ changes to the conditions of preparing and storing the samples.

INTRODUCTION

One of the factors exerting an essential influence on physicochemical and catalytic properties of polycrystalline oxide catalysts is their defect structure and coverage with the adsorbed oxygen. Owing to complexity of the relationships between biography of polycrystalline preparations of semi-conducting oxides and their physicochemical properties, studies of this problem are in most cases carried out on model systems. One of them is nickel oxide—an oxide semiconductor of *p*-type. The investigations are carried out with polycrystalline NiO, obtained by thermal decomposition of salts such as carbonates, nitrates, or by thermal decomposition of nickel hydroxide. The decomposition is conducted in the atmosphere of air or in a vacuum. The oxide obtained in the latter case shows the ratio of number of oxygen atoms to the number of nickel atoms Ni:O = 1:1, within the accuracy of analytical methods. It was observed that the properties of NiO prepared in vacuum (1–4) are considerably differ-

ent from those of the preparations obtained by thermal decomposition of nickel salt in the atmosphere of air (5, 6). The present work is concerned with the latter type of the preparations.

The stoichiometric composition of NiO is determined usually by chemical analysis, or in some cases it can be derived from the results of magnetic measurements (4). There have been described a number of analytical methods for determination of the deviations from stoichiometry in NiO. They may be divided into two groups:

i. Indirect methods. They consist in determination of the total amount of oxygen or nickel in a sample of the oxide. The content of excess oxygen is found from the difference in mass of the weighed amount of the oxide and the mass of stoichiometric oxide calculated from the analytical results. The most important of these methods are: (a) gravimetric analysis, in which nickel contained in the sample is determined as a complex with dimethylglyoxime, (b) reductometric analysis consisting in reduction of the oxide

with hydrogen and weighing the water hence formed after its adsorption on silica gel, (c) complexometric analysis, employing the reaction of nickel with EDTA after dissolving the oxide sample.

ii. Direct Methods. These make use of the high oxidizing potential of the Ni^{3+} ions. In these types of analyses the sample is dissolved in an acid (most often in HCl) in the presence of a reducing agent. From the quantitative analysis of products of the redox reaction, the content of the excess oxygen is found. The most important of these methods are: (a) iodometric method in which iodide ions are a reductant. They are oxidized during dissolving the sample and the iodine evolved is determined with thiosulfate, (b) Bunsen-Rupp method—chloride ions from concentrated HCl are a reductant. The chlorine evolved is distilled off and absorbed in the solution of potassium iodide, and the iodine evolved is determined with thiosulfate, (c) manganometric method— Fe^{2+} ions are a reductant. The excess of these ions remaining after the reaction is titrated with permanganate. Beside the Fe^{2+} ions, also arsenite ions or oxalic acid are used as reducing agents.

It turned out that the data on stoichiometric composition of NiO preparations obtained by decomposition of nickel salts in air, reported by various authors differ considerably. Since problems of accuracy in determinations of stoichiometric composition and reproducibility of analytical results is of great importance in physico-chemical studies, it seemed interesting to analyze the existing discrepancies.

Another problem considered in the present work concerns the differences in stoichiometric composition of the bulk of crystals and their surface layers. These differences may be related first of all to chemisorption of oxygen taking place on the surface of nickel oxide. The effect of defect structure on chemisorptive properties of NiO are consequently also discussed.

I. DETERMINATION OF DEVIATIONS FROM STOICHIOMETRY IN NiO

1. General Remarks

All the chemical methods described in the literature for determination of devi-

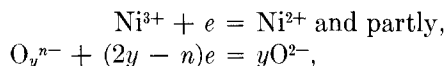
ations from stoichiometry in NiO are based on certain assumptions, the most important of which can be summarized as follows:

1. The sample is composed solely of nickel and oxygen, i.e., it does not contain any impurities or adsorbed water, and

2a. The reduction of oxygen occurs quantitatively (indirect methods), or

2b. The following equity is preserved: 2 Ni^{3+} ions which oxidize 2 I^- ions into I_2 molecule are supposed to be equivalent to $\text{O}_{\text{excess}}^{2-}$ or $2\text{O}_{\text{excess}}^-$ or $2\text{O}_{\frac{1}{2}\text{excess}}^-$ (direct methods).

Simplifying the problem to nickel oxide free from the chemisorbed oxygen, one may state that the main difference between direct and indirect methods lies in the fact that in the latter case it is the number of excess oxygen atoms which is determined; whereas, in the case of direct methods the determinations yield the number of Ni^{3+} ion. In the case of NiO samples covered with oxygen, ionosorbed oxygen present on the surface of NiO may occur in several forms differing by the number of electrons (taken per one oxygen atom) supplied by the crystalline lattice. In the case of direct method the electrons supplied by chloride or iodide ions during dissolving the oxide in an acid may be used up in the following processes:



where O_y^{n-} denotes any form of ionosorbed oxygen less reduced than O^{2-} (e.g., O^- , $\text{O}_2^- \dots$).

Assuming that the number of atoms of excess oxygen is equal to the number of all oxygen atoms present in the weighed amount of NiO, irrespectively of the form of their occurrence and the mode of oxygen bonding, diminished by the number of nickel atoms, then the indirect method should in principle give correct results, whereas the direct methods—the results lower by the amount of oxygen which does not react with Cl^- or I^- ions (i.e., the oxygen adsorbed in the form of neutral atoms or molecules). The term “excess oxygen” may be applied solely to the oxygen present in the crystalline lattice of NiO, or on its surface in the ionosorbed form, which cause

the formation of the appropriate number of the Ni^{3+} ions. In this case the indirect methods should give higher results and the direct method the correct ones. The latter results may be somewhat higher owing to the fact that the part of the adsorbed molecules of O_2 may not be evolved as a gas during dissolving in the acid, but may react with the reducing agent.

We propose to employ the term "excess oxygen" for describing only this part of oxygen ions present in the lattice (in the bulk) of the oxide, which causes formation of the appropriate number of the Ni^{3+} ions i.e., excess oxygen $\hat{=}$ lattice excess oxygen. For the sum of the lattice excess oxygen and surface excess oxygen i.e., ionosorbed oxygen, we propose the term "active oxygen," i.e.,

active oxygen $\hat{=}$ excess oxygen
+ surface excess oxygen.

We suggest also to neglect oxygen adsorbed without exchange of electrons between gas and solid phase in calculations of deviations from stoichiometry. Lack of clear and unambiguous definitions leads to misunderstanding.

2. Results of Analyses and Discussion

To compare the results of determinations of stoichiometric composition of NiO , the data reported by various authors are summarized in Table 1. Table 1 gives the results for preparations of NiO obtained by thermal decomposition of nitrates and carbonates conducted in air at various temperatures of annealing. Items 1-10 show the results obtained with indirect methods, items 11-18 with direct methods.

As shown in Table 1 there exist, in some cases, considerable differences in the data reported for the preparations annealed at a given temperature by different authors. They are most distinct for the samples annealed at higher temperatures. This is due to the fact that deviation from stoichiometry are in these preparations very small, being close to the sensitivity of analytical methods. If in spite of the existing differences the mean value (\bar{d}) is determined for different temperatures of annealing, and the ratio of the mean values

obtained by the two groups of the analytical methods ($f = \bar{d}_1/\bar{d}_2$) is calculated, it appears then that the results obtained by the direct methods are 1-2 orders of magnitude lower than the results obtained by the indirect methods. One of the reasons for these differences is provided, as it has been already mentioned, by the differences in definition of the term "excess oxygen." In the case of analyses done by the indirect methods the determination comprises, in addition to the lattice excess oxygen and surface excess oxygen, also oxygen adsorbed physically. The direct methods on the other hand yield only the sum: lattice + surface excess oxygen, i.e., active oxygen. Such source of differences in the analytical results was pointed out by Maxim and Braun (11).

In the case of direct analyses of NiO samples obtained and stored in the atmosphere of air, the determinations comprise also two components. The results of the analysis is averaged, on the other hand, over the total weighed amount. Attention was drawn to this fact in 1961, and the appropriate method allowing separation of these components was described (19). Obviously the direct methods cannot be employed for determination of the form in which surface excess oxygen exists. The possibility of determination of the form of the chemisorbed oxygen by application of the suitable modified Bunsen-Rupp method was recently considered by Bielański (20).

The differences in the values obtained by different authors with the same methods are caused, in our opinion, by the different conditions of preparing and storing of the samples. It has been observed, for instance, that even comparatively small changes in the preparative conditions (e.g., annealing in the crucibles partly closed or open, or in a stream of air) may influence markedly the stoichiometric composition of the preparations. In the majority of papers such details of the preparation procedure were not given. The way of storing the preparations and the rate of their cooling from the annealing temperature to the room temperature may not be quite indifferent either, for the results obtained.

Another reason for the discrepancies be-

TABLE 1^a

Ref.	Sam- ple origin	Time of an- neal- ing (hr)	Method of analysis	Oxygen (At. %) above the molar ratio Ni:O = 1:1; Temp of annealing:							
				300	400	500	600	700	800	900	1000
1. Shimomura <i>et al.</i> (7)	n	2	grav	—	—	20.0 ^b	9.0 ^b	—	5.0	2.0	0.33 ^b
2. Ida (8)	c	5	red	—	10.0	4.0	1.0	—	—	—	—
3. Szirokov <i>et al.</i> (9)	c	5-7	grav	28.0	17.4	8.3	7.4	7.4	6.6	—	2.9
4.	n	5-7	grav	10.7	9.9	9.1	5.7	5.7	2.0	—	3.1
5. Kutseva (10)	c	3	red	—	—	11.5	—	6.5	—	—	—
6. Maxim and Braun (11)	c		grav	13.6	9.5	5.7	1.9	0.5	—	—	—
7. Mechandjiev and Bliznakov (12)	c	3	grav compl	30.6	19.4	16.0	5.7	3.8	2.9	1.0	0.0
8. Bliznakov <i>et al.</i> (13)	c	24	compl	—	17.4	13.8	—	5.7	—	—	0.0
9.	c	24	red	—	18.0	13.0	—	5.7	—	—	0.0
10.	c	24	red v	—	16.7	12.3	—	5.7	—	—	0.0
		d ₁ :		20.8	14.8	10.4	4.3	5.1	4.1	1.5	0.9
11. Parravano (14)	n	4	iod	—	—	—	—	—	—	0.33	—
12. Ida (8)	c	5	iod	—	0.5	0.205	0.155	0.135	0.055	—	—
13. Maxim <i>et al.</i> (11)	c		iod	1.2	0.9	0.5	0.3	0.07	—	—	—
14. Yamashina and Sano (16)	n	5	iod	—	—	0.19	—	—	—	—	—
15. Yamashina and Nagamatsuya (15)	n	5	iod	—	—	0.04	—	—	—	—	—
16. Nachman <i>et al.</i> (17)	c	2	iod	—	—	—	0.097	0.037	0.025	0.007	0.002
17. Bliznakov <i>et al.</i> (13)	c	24	iod	—	0.665	0.450	—	0.114	—	—	0.178
18. Uchijima <i>et al.</i> (18)	c	8	iod	1.82 ^b	1.53	0.62	0.30	0.2	—	0.1	—
		d ₂ :		1.2	0.9	0.3	0.2	0.1	0.04	0.15	0.09
		f = d ₂ /d ₁ :		0.06	0.06	0.03	0.05	0.02	0.01	0.1	.01

^a Abbreviations: n, nitrate; c, carbonate; grav, gravimetric; red, reductometric; compl, complexometric; red v, reduction in vacuum; and iod, iodometric method, all modifications.

^b Value 50°C higher.

tween the values obtained by different authors with the same methods lies in the presence of impurities in the samples. Any preparation of NiO, even free from im-

purities like oxides of other metals, CO₂, NO₂, etc., contains water on its surface. In 1926, Le Blanc and Sachse (21) stated that the preparation of NiO annealed at 550°C

contained 1.3 wt % of water; and it has been found in our experiments that the preparation obtained by annealing of nickel carbonate at 1000°C, exposed to humid air, absorbs water up to 0.2% of its weight. Assuming, for instance, that the preparation contains 1.3 wt % H₂O which is not taken into account in the analysis with an indirect method, then it will result in obtaining values: of 5.8 at. % in gravimetric and complexometric methods and 5.2 at. % in reductometric method. The arithmetic mean of results reported by different authors (see Table 1) for preparations obtained at 500°C amounts to 10.4 at. %, and for preparations obtained at 600°C to 4.3 at. %. Then it can be supposed that water contributes considerably to the value determined by indirect methods. In the determinations carried out by the direct method, the same amount of water does not influence practically the result of the analysis. For the water content of 1.3 wt % and active oxygen content of 0.5 mg/1 g of the sample (about 0.2 at. %) the difference in the results of the analyses taking, and not taking, into account the presence of water amounts to 0.002 at. %, which is usually below the limits of the sensitivity of the method. In the light of the above given facts the conclusion drawn earlier concerning the comparison of the results obtained by different methods (13, 22) should be treated with caution.

On the other hand, it has been found that during decomposition of the Ni₂O₃·xH₂O preparations, practically the total amount of the active oxygen is evolved simultaneously with water (23). It can be hence supposed that water, present in the preparations of NiO, exhibits also certain influence on the content of the Ni³⁺ ions in the preparation. If this is the case, then the water content in the preparations should be controlled also in direct analyses. The different content of water may be, for instance—amongst the other factors—responsible for considerable scattering of the experimental values in iodometric determinations (cf. Table 1).

In the earlier work (24), the authors, applying a number of variants of direct

methods to the analysis of stoichiometric composition (active oxygen content) of the same preparation of the approximate composition 2NiO·O·4H₂O, have shown, that all of them led to the very close results (Table 2). The choice of the preparation

TABLE 2

Method	Mean amount of active oxygen (at. %)	SD
Iodometric	26.65	±0.024
Bunsen-Rupp I ^a	26.01	±0.066
Bunsen-Rupp II ^b	26.17	±0.043
Manganometric (with Fe ²⁺ ions)	26.50	±0.022

^a Modification with silicon grease vessel.

^b Modification without grease.

for testing the analytical methods was dictated by its high content of active oxygen. The good agreement between the results obtained by various variants of the direct methods, in particular between iodometric and manganometric, is observed.

II. EFFECT OF BIOGRAPHY OF NiO ON ITS CHEMISORPTIVE PROPERTIES

1. The Experimental Method and Results of Analyses

The analytical method which makes possible to determine the content of (lattice) excess oxygen and the surface excess oxygen in the sample consists in performing the classical analysis with the Bunsen-Rupp method and independently, the Bunsen-Rupp analysis after degassing the sample at elevated temperature (19). The results of the first analysis yield the content of the active oxygen, whereas those of the second—the content of the excess oxygen. It was found that the surface excess oxygen constitutes the major part of the active oxygen. In Table 3 the data obtained with the help of this method by Bielański and co-workers (26–29) and Dereñ *et al.* (30) for a number of series of the preparations (obtained by decomposition of nitrate and

carbonate of nickel) annealed in the temperature range 400–1000°C, are compared.

The direct determination of the surface excess oxygen is also possible with the method reported by Uchijima *et al.* (25),

consisting in reduction of this oxygen with aqueous solution of hydrazine. The data obtained by these authors are also given in Table 3.

To compare the results obtained previ-

TABLE 3^a

Temp (°C)	R: Or: hr:	18 c 5	26 c 5	27 n 5	28 c 2	29 c	30 c 2	30 c 2	30 c 2
300	A	1.82	—	—	—	—	—	—	—
	E	1.27	—	—	—	—	—	—	—
	S	121	—	—	—	—	—	—	—
	θ	8.5	—	—	—	—	—	—	—
400	A	1.52	1.175	1.50	—	2.23	—	—	—
	E	0.70	1.175	—	—	1.64	—	—	—
	S	57.6	61.3	4.57	—	224	—	—	—
	θ	10	13.5	—	—	5.9	—	—	—
450	A	1.05	—	—	—	—	—	—	—
	E	0.58	—	—	—	—	—	—	—
	S	34.4	—	—	—	—	—	—	—
	θ	13.8	—	—	—	—	—	—	—
500	A	0.62	0.24	0.86	0.42	1.55	0.24	0.43	0.47
	E	0.46	0.24	0.14	0.42	0.97	0.24	0.43	0.46
	S	26.1	7.7	2.87	14.8	113	7.7	24.0	22.3
	θ	14.6	22.5	35.1	20.7	6.9	2.3	13	15
550	A	0.38	—	—	—	0.89	—	—	—
	E	0.35	—	—	—	0.47	—	—	—
	S	17.4	—	—	—	34	—	—	—
	θ	16.6	—	—	—	11.1	—	—	—
600	A	0.31	0.14	0.17	0.19	0.15	0.14	0.25	0.27
	E	0.30	0.14	0.096	0.19	0.11	0.14	0.24	0.27
	S	14.4	2.7	1.6	4.2	6.1	3.0	8.1	7.1
	θ	17.4	36.9	43.2	32.4	14.5	33	22	28
700	A	0.2	0.058	0.135	0.10	—	0.09	0.14	0.09
	E	0.2	0.058	0.085	0.10	—	0.09	0.13	0.09
	S	8.8	2.6	1.57	2.1	—	2.6	5.5	3.5
	θ	19.3	30.6	21.8	36.9	—	25	18	19
800	A	—	0.042	0.072	0.05	0.06	0.04	0.07	0.06
	E	—	0.042	0.072	0.05	0.03	0.04	0.05	0.06
	S	—	1.8	1.26	0.8	0.5	1.8	2.4	2.0
	θ	—	17.1	41.4	45	48.4	17	16	22
900	A	0.1	0.017	0.062	0.02	—	0.02	0.04	0.04
	E	0.1	0.017	0.062	0.02	—	0.02	0.04	0.04
	S	3.7	1.4	0.88	0.5	—	1.4	1.9	1.8
	θ	16.5	9	51.3	36	—	9	14	15
1000	A	—	nd	0.042	0.01	—	0.02	0.02	0.02
	E	—	nd	0.042	0.01	—	—	—	0.02
	S	—	—	0.75	0.3	—	0.5	0.9	1.1
	θ	—	—	41.4	28.8	—	—	—	12

^a R, references; Or, sample origin; hr, time of annealing (hours); c, carbonate; n, nitrate; A, amount of active oxygen (at. %); E, surface excess oxygen (at. %); S, surface area (m² g⁻¹); θ , surface coverage.

ously by the modified Bunsen-Rupp method (19) with the results obtained with method proposed by Uchijima (18, 25), the studies on the stoichiometric composition of the same series of preparations were performed using these two methods. The preparations were obtained by decomposition and annealing of nickel carbonate at appropriate temperatures (400–1000°C) for 5 hrs. After termination of the annealing, the preparations were cooled down to the room temperature by their removal from the oven. The annealing was done in a sillite oven in closed crucibles. The results obtained are summarized in Table 4.

The values of the oxygen coverage θ given in Tables 3 and 4 correspond to a

surface excess oxygen may be also considered in terms of chemisorption.

On the basis of the data given in Table 3 the dependence of the oxygen coverage θ on the annealing temperature is plotted in Fig. 1. The same dependence for series of preparations studied by us (Table 4) is illustrated in Fig. 2. Curve I corresponds to the value obtained by the modified Bunsen-Rupp method; and curve II, to the value obtained for the same series of preparations by the Uchijima method.

2. Discussion of the Results

a. Comparison of the analytical methods.

As shown in Fig. 2, both Uchijima and Bunsen-Rupp methods give the same course

TABLE 4

Temp of annealing (°C)	Surface area (m ² /g)	Mean amount of active oxygen (at. %)				Surface coverage (%)	
		Hydrazine method; surface ex- cess oxygen	Bunsen-Rupp method			Bunsen-Rupp method	Hydrazine method
			Active oxygen	Excess oxygen	Surface ex- cess oxygen		
1	2	3	4	5	6	7	8
400	139.6	1.03	1.44	0.57	0.87	4.5	5.4
500	38.5	0.34	0.56	0.29	0.27	5.2	6.4
600	10.6	0.12	0.26	0.17	0.09	6.2	8.2
700	3.37	0.10	0.16	0.11	0.05	10.8	21.7
800	1.24	0.031	0.08	0.03	0.05	29.4	16.2
900	1.19	0.010	0.08	0.02	0.06	36.8	6.1
1000	0.28	0.001	0.012	0.007	0.005	13.0	2.6

fraction of a monolayer, with the assumption that the surface of crystalline samples of NiO is composed in equal proportions of planes (100) and (110), and that one surface excess oxygen atom corresponds to two Ni³⁺ ions. Such an assumption is fully applicable to lattice excess oxygen; however, it is less correct in the case of the surface excess oxygen. Chemisorption of oxygen results rather in formation of O₂⁻ or O⁻ ions than in the formation of O²⁻ ions, and we may suppose that the "true" amount of oxygen chemisorbed at a unit surface area (determined by krypton BET method) is larger than that given by the analysis. Nevertheless it seems that these data may be taken as a certain measure of the concentration of chemisorbed oxygen. Hence,

of the dependence of the oxygen coverage on the annealing temperature. The values obtained with these two methods for a given temperature of annealing are also close, one to another.

It is noteworthy that this agreement is much better for the samples annealed at lower temperatures than for those annealed at higher temperatures. One could have anticipated the reverse effect. At lower temperatures the surface of the preparations is better developed and hence "penetration" of the aqueous solution of hydrazine in the pores might be more difficult. It is not possible at present to explain the reasons for the discrepancies in the results obtained for the samples annealed at higher temperatures.

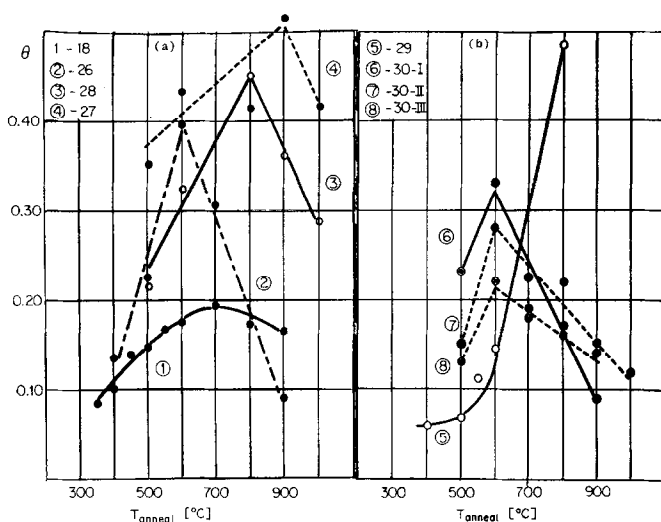


FIG. 1. Dependence of oxygen coverage θ on the annealing temperature (data from the literature).

We would like to draw attention to the modification of the Bunsen-Rupp method described in (19) was based on the two assumptions:

(a) degassing of the sample at 400°C leads to the practically complete removal of the chemisorbed oxygen, and

(b) heating of the sample at this temperature during the oxygen desorption does not alter the stoichiometric composition of the bulk of crystals. The latter assump-

tion is equivalent to the statement that diffusion of ions from the bulk of crystallites towards the surface is at 400°C too slow to affect the stoichiometric composition of the bulk of the samples. In the case of the method proposed by Uchijima, no additional assumptions are required. Comparatively good agreement of the results obtained by the described two methods constitutes, therefore, an additional proof for the correctness of the assumptions made.

b. Possibility of derivation of specific surface area of NiO from the results of chemical analysis. On the basis of previously reported data (19), Peers (31) assuming the independence of the oxygen coverage of NiO preparations of the temperature of annealing, has given an expression for calculation of the specific surface area S from analysis of the active oxygen content P (at. %). Since value of P is for the majority of samples annealed at temperatures higher than 500°C, practically equal to surface excess oxygen, Peers assumed that this value may be taken as a good measure of these contents:

$$\log S = \log P + 1.55.$$

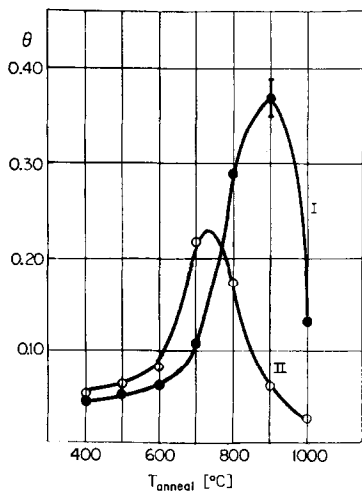


FIG. 2. Dependence of oxygen coverage θ on the annealing temperature: (Curve I) results obtained with the Bunsen-Rupp method; (Curve II) results obtained with the hydrazine method.

The data summarized in Tables 3 and 4 show that the coverage with oxygen θ is dependent on the temperature of the previous annealing and also that the plot of

the function $\log P = f(T_{\text{ann}})$ yields in the investigated range a straight line; whereas, the plot $\log S = f(T_{\text{ann}})$ may be described approximately by two straight lines. This means that the relation between these three parameters, which for small values of P can be described by the formula,

$$S = 730 \frac{P}{\theta},$$

is essentially a function of three variables. The method proposed by Peers for determination of the specific area of NiO from the analysis of active oxygen, or surface excess oxygen content leads, in the light of the above shown facts, only to the rough results. The error (standard deviation) of $\log S$ values, estimated from our measurements amounts to ± 0.36 .

c. Dependence of stoichiometric composition of NiO (excess oxygen content) on the annealing temperature. The present results show that the deviation from stoichiometry in the bulk of NiO crystallites (i.e., the excess oxygen content) decreases with the increase in temperature of previous annealing of the samples (see Tables 3 and 4). This fact may be explained taking into consideration the thermodynamic data concerning the dependence of defect structure of NiO on temperature as follows:

In the case of preparations obtained by decomposition in air of appropriate salts carried out at lower temperatures, the oxides obtained may be regarded as supersaturated solutions of Ni_2O_3 in NiO. With the increase in the annealing temperature, the system approaches the state of equilibrium, which is characterized by markedly lower concentration of the excess oxygen. This is illustrated schematically in Fig. 3. Curve I in Fig. 3 gives the changes of the excess oxygen concentration as a function of the annealing temperature; curve II, changes of the equilibrium concentration of the excess oxygen as a function of the same parameters. With the increase in this temperature the system approaches the equilibrium. Since formation of the defects is an endothermic process, it can be expected that beginning from a certain comparatively high temperature, the excess oxygen content

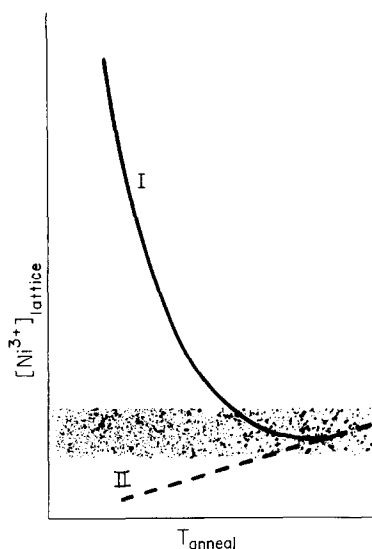


FIG. 3. Schematic course of the excess oxygen changes with the change in the annealing temperature: (Curve I) the course observed for preparations of NiO obtained by decomposition of salts at a given temperature; (Curve II) changes in the equilibrium excess oxygen concentration in NiO; (shaded band) sensitivity limit of analytical methods.

should begin to increase. Unfortunately, owing to the very low value of the equilibrium concentration, the latter conclusion cannot be confirmed experimentally with the help of chemical methods, the sensitivity of these methods (about 0.01 at. %) being too low. The sensitivity of the analytical method is denoted in Fig. 3 by a shaded band. According to Mitoff (32) the equilibrium concentration of Ni^{3+} ions in the NiO lattice at the temperature of 1000°C amounts to 2.10^{-4} ions/pair of ions.

d. Dependence of chemisorptive properties of NiO on the annealing temperature.

When considering the dependence of the coverage of the NiO surface with chemisorbed oxygen, i.e., the problem of the surface excess oxygen content as a function of the temperature of previous annealing, two facts should be taken into account:

a. The chemisorption isobar of oxygen on NiO prepared by decomposition of carbonate at 500°C , determined by Haber and Stone (33) shows a maximum at the temperature of about 300°C . At the same tem-

perature the maximum is observed for the samples obtained by decomposition of the carbonate at 900 and 1000°C (34).

b. The second fact is related to the time of establishing the surface equilibrium. As it was shown previously in the measurements of the electron work function, the chemisorptive equilibrium of oxygen on the surface of polycrystalline NiO at 400°C is established during the time not exceeding 5 min (35, 36).

In the light of this fact it may be assumed that:

a. In the case of all the samples considered, the temperature of isobar maximum is approximately the same, amounting to about 300°C, and

b. Chemisorption equilibrium at temperatures above 400°C is established very fast for all the samples. In all described cases the samples were obtained by annealing and fast cooling down to the room temperature at which the analyses were performed. Thus it may be supposed that values of the surface excess oxygen for the sample annealed at a given temperature correspond to the value of coverage θ_{\max} at the temperature of isobar maximum.

Taking this into account, it appears that the dependence of the coverage with chemisorbed oxygen on the temperature of previous annealing determined analytically, is related to the change in the intrinsic defect structure of the crystalline lattice of NiO occurring during the annealing. Depending on the annealing temperature, the preparations are obtained of the different concentrations of the Ni³⁺ ions in the crystalline lattice (cf. Fig. 3). It seems plausible that this fact may be related to different coverage at the maximum of chemisorption isobar. Such interpretation is shown schematically in Fig. 4. The curves in Fig. 4a illustrate the course of isobars for series of preparations annealed at different temperatures, and the curve in Fig. 4b, the expected course of the analytically found coverage of the surface excess oxygen at room temperatures as a function of the temperature of previous annealing.

This interpretation of the results obtained provokes a question why a mono-

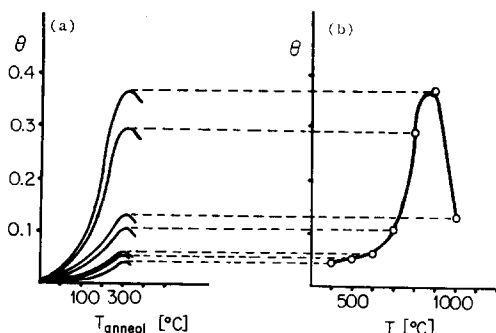


FIG. 4. Oxygen adsorption isobar on NiO: $\theta = f(T)$: (a) group of isobars corresponding to different states of the preparation surface caused by different temperatures of annealing; (b) present experimental results corresponding to the assumption about changes in the surface properties in the course of the temperature changes.

tonic decrease of the defect concentration of the crystalline lattice of NiO with the increase in the annealing temperature (cf. Fig. 4) causes an unmonotonic change of the coverage with the chemisorbed oxygen. Analogous phenomena have been encountered in catalytic studies and is known as catalyst modification.¹

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¹The possible interpretation is given in J. DEREŃ, Y. ZIÓŁKOWSKI, AND E. BALUCH, *Bull. Acad. Pol. Sci., Ser. Sci. Chim.* (in press).

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