

REDUCTION OF MIXED NiO-ZnO OXIDES WITH INCORPORATED RADIONUCLIDE ^{65}Zn BY HYDROGEN

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Received November 28th, 1973

Reduction of mixed nickel and zinc oxides by hydrogen has been studied thermogravimetrically. Samples of various composition with incorporated ^{65}Zn were prepared by calcinating coprecipitated basic carbonates of both components at 400°C in air. The initial specific activity was $3 \text{ mCi/g} \pm \pm 15\%$, the samples selected were prepared with specific activities of 0.87 and 22.5 mCi/g, respectively. Effect of radiation proper of the system manifests itself in a slow-down of the rate of reduction and in the increase of its apparent activation energy at low specific activities already. The effect may be observed up to the temperature of 440°C and can be explained by a shift of equilibrium among different forms of adsorbed superstoichiometric oxygen of nickel oxide. Position of this equilibrium may be affected by a heat treatment of samples in the inert atmosphere before the reaction itself. At higher specific activities, an inversion of the effect takes place, the reduction proceeds at higher rate and with lower activation energy than with inactive samples. The kinetics of reduction of samples of both series can be described by an equation derived for zonal model of the decomposition of solids.

In previous papers^{1,2}, reduction of mixed nickel and zinc oxides by hydrogen was systematically studied. Primary attention was paid to the effect of different genesis and conditions of the preparation of the two-component oxides upon the process of reduction. The effect of ionizing radiation on the reduction of nickel oxide by hydrogen was studied by Simnad and coworkers³. The oxide samples prepared by oxidation of small nickel sheets of high purity were prior to reduction irradiated with protons of energy 260 MeV, using a flow of 10^{16} protons/cm². 2–3 times higher rate of reduction and 3–4 times shorter induction period, as compared with equal nonirradiated samples, was found. The effect was observable up to a temperature of 400°C . An opposite effect of radiation on the reduction of nickel oxide prepared by decomposing nitrate at 500°C in air was observed by Yamashina and Nagamatsuya⁴. For samples irradiated by ^{60}Co with an exposure of $1 \cdot 10^7 - 2 \cdot 10^8 \text{ r}$, extension of the induction period and decrease of the rate of reduction by hydrogen took place.

In order to study effect of radiation of incorporated ^{65}Zn radionuclide, two series of mixed nickel and zinc oxides of different ratio of representation of both components within 0–100 mol per cent were prepared in this paper. The standards will be denoted as samples of inactive series, while samples with incorporated radionuclide as samples of the active series. Reduction of oxides of the two series under equal experimental conditions has been studied and comparison of the results has been made.

TABLE I
Specification, Composition, and Specific Surface Areas S_1 of Samples of Inactive Series

Sample	Weight %		Mol. %		S_1 m ² /g
	Ni	Zn	NiO	ZnO	
1	74.98	—	100.00	—	28.39
2	70.67	6.08	94.30	5.70	22.72
3	68.25	6.84	91.52	8.48	30.18
4	60.61	13.78	83.10	16.90	45.77
5	52.94	22.14	72.75	27.25	48.40
6	43.07	31.56	60.40	39.60	51.38
7	36.53	38.23	51.48	48.52	50.73
8	29.12	45.64	42.20	57.80	55.02
9	22.70	51.43	32.95	67.05	59.92
10	18.61	54.83	27.46	73.54	72.94
11	11.44	63.19	16.78	83.22	66.87
12	6.07	69.17	8.89	91.11	51.29
13	0.98	75.09	1.13	98.87	37.78
14	—	78.54	—	100.00	19.34

TABLE II
Specification, Composition, and Specific Surface Areas S_2 of Samples of Active Series

Sample	Weight %		Mol. %		S_2 m ² /g
	Ni	Zn	NiO	ZnO	
1	70.00	6.39	92.96	7.04	13.7
2	68.80	7.57	91.40	8.60	20.74
3	61.00	15.00	82.53	17.47	24.60
4	49.20	27.60	66.40	33.60	34.32
5	47.80	30.00	63.77	36.23	38.12
6	35.50	41.90	48.38	51.62	27.20
7	23.10	52.20	33.62	66.38	68.84
8	21.80	55.40	30.57	69.43	31.19
9	16.00	61.80	22.31	77.69	23.60
10	10.92	67.40	14.87	85.13	60.90
11	4.05	75.97	5.73	94.27	42.40
12	1.40	79.12	1.64	98.36	15.40
13	—	77.01	—	100.00	68.10
A	23.79	55.54	32.25	67.75	63.26
B	11.62	64.60	16.23	83.77	50.85

Specific activity mCi/g: 1 to 13 is $3 \pm 15\%$; A 0.87; B 22.55.

EXPERIMENTAL

The oxides of both series were prepared by calcinating basic carbonates which were produced by precipitating nitrate solutions of both metals with potassium carbonate solution in 15% excess with respect to stoichiometry. The concentration of all the solutions was 1 mol l^{-1} , the reagents were of A.R. purity. The precipitation was carried out under vigorous stirring and at a temperature of 20°C by dropwise addition of all three solutions simultaneously into 200 ml redistilled water. The precipitate was decanted and washed on filter with redistilled water till no nitrates could be detected. During preparation of samples of the active series, radioactive ^{65}Zn isotope likewise in the form of a nitrate solution was prior to precipitation added to the solution of starting zinc nitrate so that all the samples may have an approximately the same specific activity. After drying for 24 hours at 20°C and for 3 hours at 120°C , the sediment of carbonates was calcinated for 6 hours at 400°C in air. The oxides of both series were analyzed for metal content complexometrically. By comparing with a standard, specific activity of samples of the active series was determined. The initial specific activity is $3 \text{ mCi/g} \pm 15\%$ for all samples of the series. To study the effect of specific activity, two samples in addition were prepared, of specific activities 0.87 and 22.55 mCi/g, respectively. Specific surface areas were measured by adsorption of nitrogen at low temperatures. Specification of the samples, their composition and magnitudes of specific surface areas are summarized in Table I for samples of the inactive series, and in Table II for those of the active series. Reduction of mixed oxides was investigated on a thermogravimetric apparatus described previously⁵, over a temperature range of $320\text{--}500^\circ\text{C}$. The conditions were found, when rate and kinetics of the reductions are independent, for the standard weight portion

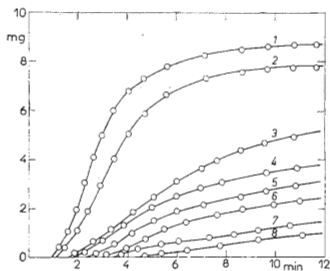


FIG. 1

Kinetics of Reduction of the Active Series Samples at 380°C

Numbers of the curves correspond to numbers of the samples of the series (Table II).

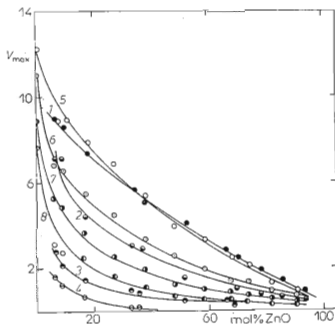


FIG. 2

Plot of Maximum Rate of Reduction (mg/min) at Different Temperatures against Composition

Active series: 1 470°C ; 2 440°C ; 3 380°C ; 4 350°C ; Inactive series: 5 480°C ; 6 430°C ; 7 370°C ; 8 350°C .

of 50 mg, of the hydrogen flow rate, for an arbitrary composition of the sample. Region of independence of this quantity is for the given arrangement guaranteed at a hydrogen flow rate of 56 ml/min, used in all the experiments.

RESULTS

It follows from Fig. 1 that with the increasing content of zinc oxide in the samples, the rate of reduction decreases and time of the induction period increases. Effect of the increasing concentration of zinc oxide with samples of inactive series similarly becomes evident. The inactive samples, however, are reduced at a higher rate, except for samples No 13 and 14 for which weight losses neither at 500°C were observed. In the active series, merely reduction of samples No 1 and 2 at a temperature of 300°C occurs, the other samples are not reduced at a measurable rate; for an observable reduction of sample No 11, minimum temperature of 470°C is needed and samples No 12 and 13 are not reduced even at 500°C. Plot of the maximum rate of reduction (V_{\max}) against composition at different temperatures (Fig. 2) shows a differing effect of temperature upon the rate of reduction. In the region of higher reduction temperatures (above 440°C), the V_{\max} values are for both series comparable. Below this temperature boundary, the V_{\max} values of the active series are situated, independently of composition and deeply below values of maximum reduction rates of the inactive series. The induction periods of reduction of active samples are particularly at lower temperatures of reduction longer than for the inactive samples of equal composition, reduced under equal conditions.

In order to exclude differences in the magnitudes of specific surface areas of individual samples in both series, values of the maximum reduction rates were related to the surface unity. It follows from the plot of this specific maximum rate of the reduction against composition of the temperature of reduction up to 400°C (Fig. 3) that even in this case the rates of reduction of active samples are under the same conditions lower.

The values of the apparent activation energy, calculated from the temperature dependence, are likewise different for both series. In the temperature range of 500 to 430°C the mean value of this quantity for inactive series amounts to 4.5 ± 3 kcal/mol over the whole range of composition and 10.2 ± 4 kcal/mol for samples of the active series. In the region of lower temperatures of 430–320°C, the activation energy of reduction is 22.8 ± 1 kcal/mol for inactive samples and 38.6 ± 2 kcal/mol for samples of the active series. It follows from analysis of experimental results according to criteria presented in the literature^{2,6} that up to 430°C reduction of samples of both series under pure kinetic conditions takes place and at higher temperatures the rate of reaction is affected by diffusion processes in its own volume phase of the samples. For both series, dependence of a relatively high variance of activation energy values upon composition for the high-temperature region is characteristic, while values

approaching the upper limit belong to samples of higher zinc oxide contents. For samples A, B of the active series, the following values of the activation energy of reduction were calculated: sample A — 18.3 kcal/mol and 43.7 kcal/mol for the temperature ranges of 500–430°C and 430–320°C, respectively, sample B — 6.6 kcal/mol (500–430°C) and 20.8 kcal/mol (430–320°C). It follows from Table III that effect of activity of the system becomes evident already at low values of the specific activity as results from a high value of the activation energy (sample A). The rate of reduction of this sample is considerably lower than for an inactive sample of the same composition. On the contrary, the sample of a high specific activity (B) is reduced at a rate comparable with that of a similar inactive sample. It further follows from this Table that at lower temperatures of reduction (380°C) the rate of reduction of this sample is the highest one under a simultaneous decrease of the apparent activation energy, although its composition (content of the NiO component capable of being reduced) virtually corresponds to composition of sample 10 which is at 380°C, no longer reduced at a measurable rate.

Effect of the heat treatment of samples in the inert atmosphere on the course of the subsequent reaction was followed for two series of the experiments. In the first case, the samples were before reduction treated for 1 hour in a special tube in a stream of dry argon at different temperatures. After the end of the treatment the samples were kept in argon till cooling down to room temperature and usual weight portions (50 mg) were reduced in a temperature range of 350–440°C. Total time interval after the end of the treatment till the start of the reduction was approximately 6 hours. Similarly as for the inactive series, under these conditions also for samples treated at 500°C, an increase of the rate of reduction as well as of value of the apparent activation energy by about 1/3 takes place, the differences in the rate

TABLE III

Specific Maximum Rate of Reduction (mg/min. m²) of Active Samples of Different Specific Activity and Temperatures

Sample	Weight % NiO	<i>E</i> kcal/mol	<i>V</i> _{s,max.}		
			500°C	440°C	380°C
A	30.21	43.7	0.05	0.015	0.002
7	29.40	38.9	0.10	0.03	0.004
B	14.79	20.8	0.04	0.02	0.005
10	13.90	—	0.02	0.007	is not reduced

The given values of apparent activation energy, *E*, of reduction are valid for kinetic region 430 to 320°C.

of reduction of samples of the active and inactive series being maintained, similarly as for the nontreated samples. At high temperatures of the treatment (700–1000°C) sintering of the surface, slow-down of the rate of reduction as well as extension of the induction period takes place.

The differences in the reduction of pre-treated oxides between the two series were established in the second series of the experiments, in which the samples were treated immediately in the reduction tube, and after finishing the treatment, reduction by admitting hydrogen was immediately started at the same temperature. The time of treatment was likewise 1 hour, temperature of reduction 410°C. Kinetics of the reduction of inactive samples treated in this way did not differ from the reduction of original samples, accomplished under equal conditions. For active samples treated in this way, however, an increase of the rate of reduction, when compared with original

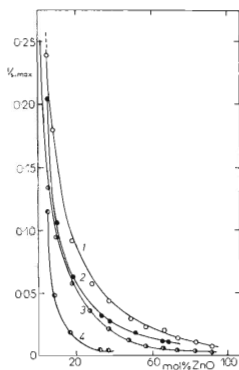


FIG. 3

Plot of Specific Maximum Rate of Reduction ($\text{mg}/\text{min m}^2$) of Samples of Inactive and Active Series against Composition at Different Temperatures

Inactive series: 1 380°C, 3 350°C; active series: 2 380°C, 4 350°C.

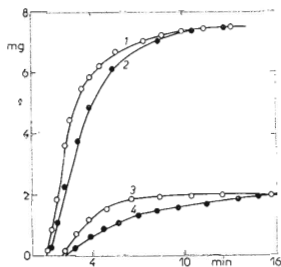


FIG. 4

Kinetics of Reduction of Treated and Nontreated Samples 3 and 9 of Active Series at 410°C

One-hour treatment in argon stream at the same temperature, reduction started immediately after the treatment. Sample 3 1 treated, 2 nontreated; Sample 9 3 treated, 4 nontreated.

samples, was observed and the entire course of the reduction approached that of the inactive samples of the same composition. The kinetics of reduction of treated as well as nontreated active samples 3 and 9 can be seen in Fig. 4.

DISCUSSION

According to results of the study of fine oxides structure of the inactive series, the system may be characterized in the region up to approx. 30 mol per cent of ZnO as a homogeneous solid solution of both components and above this concentration as a two-phase system consisting of a solid solution with original cubic lattice of NiO and free zinc oxide². Maximum influence of the electron structure of both oxides occurs then in the first region, which becomes evident also in a maximum change in the rate of reduction with the increasing zinc oxide content up to the concentration quoted (Fig. 2 and 3). The observed steep decrease of the rate of reduction up to the amount of 30 mol % of ZnO incorporated in the nickel oxide lattice may be satisfactorily explained² in agreement with conceptions of the electron theory of adsorption on semiconductors⁷ with respect to the semiconducting nature of both oxides present in the system. The effect of zinc oxide and its increasing concentration in the samples on the rate of reduction becomes then evident in the same way for samples of the active and inactive series and in the same character of the dependence of the reduction rate upon composition.

It has been further shown in paper² that in addition to nickel oxide, also the second component, zinc oxide, present in the region of its excess as a separate phase, is for the inactive series partially reduced particularly at higher temperatures of the reduction. Internal transport processes and the material transport of the components reduced, manifesting themselves in the incorporation of the reduced zinc oxide portion into the nickel lattice under a simultaneous increase of the magnitude of the lattice constant of nickel, are for the rate a controlling stage in the region of high reduction temperatures, the stage being characterized by a low value of the activation energy of reduction of the samples of both series. For the active series, a partial reduction of zinc oxide may be likewise assumed, similarly as for the inactive series. Experimental weight losses achieved during reduction at 500°C, when these losses for the given sample are constant at the times of observation, were compared with theoretical losses. The latter were calculated with respect to the weight portion and composition of samples, provided that nickel oxide is the only component of the system, that is reduced. The reduction proceeds also with the active samples up to a higher degree than it would correspond to the reduction of the whole nickel oxide present in the sample (Fig. 5). The curve showing dependence of percentage of the reduction above a theoretical value upon composition attains maximum at approx. 70 mol% of ZnO. In Debye patterns of the reduced samples of the inactive series, the set of selective

reflexion belonging to an alloy of both metals, attains a maximum at the given zinc oxide content².

Kinetics of the reduction of samples of both series fits up to 430°C equation $1 - (1 - \alpha)^{1/3} = k \cdot t$, where α is the degree of reduction in time t , and k is the constant. The reduction of active as well as inactive samples proceeds then according to zonal model of the decomposition of solids.

An essential difference between the active and inactive series of the mixed oxides studied is therefore in different rates and activation energies of the reduction of samples of both series. The radionuclide ^{65}Zn employed changes into the inactive nuclide ^{65}Cu according to equation $^{65}_{30}\text{Zn} \rightarrow ^{65}_{29}\text{Cu} + \text{}^0_{+1}\text{e}$, whose accumulation in the system means an increase of concentration of the third component. According to quantitative estimation of the produced amount of this admixture, with respect to initial specific activity and time finishing preparation of the samples till the own study of the reduction, the concentration of copper produced lies below the concentration limit of copper present in the reagents employed so that the effect of copper upon kinetics of the reaction may be considered negligible.

If value of the specific maximum rate of reduction is the examined quantity that makes both series different, its percentual change, Δ , characterizing effect of the activity of the system, can be expressed by means of relationship

$$\Delta = 100 \cdot \frac{V_{s,\text{max.}}^+ - V_{s,\text{max.}}}{V_{s,\text{max.}}}, \quad (1)$$

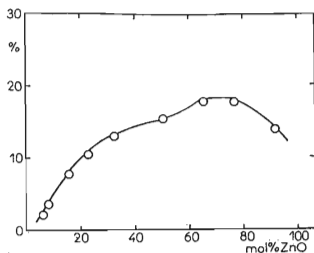


FIG. 5

Dependence of Percentage of Reduction at 500°C upon Composition above the Value Calculated Theoretically, Corresponding to Total reduction of NiO of the Active Series

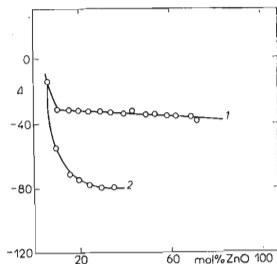


FIG. 6

Plot of Magnitude Δ (%) against Composition at Different Temperatures of Reduction
1 380°C, 2 350°C.

where $V_{s,\max}^+$ and $V_{s,\max}$ relate to active and inactive samples, respectively. Plots of value Δ against composition (Fig. 6) show that a negative effect of radioactivity of the system is involved (lower rates of reduction of active samples), which attains at a low temperature of reduction a value as high as 80% and decreases with increasing temperature of the reduction. Provided that adsorption of the reducing gas on the surface or on active centres will be a step determining rate in the kinetic region, the influence on the surface state and on adsorption properties of the system will play a decisive role. In view of the conditions of preparation of the oxides studied (calcination in air), presence of superstoichiometric oxygen of nickel oxide may be assumed in the system, while the low-temperature calcination up to 500°C leads predominantly to chemisorption of oxygen in neutral form O^0 and only to a less extent⁸ in ionogen form O^- . Effect of ionizing radiation can provide a change in equilibrium between various forms of superstoichiometric oxygen in favour of the ionogen form by the following mechanism. Localized free acceptor levels produced in the energy gap of a semiconductor by neutral adsorbed form, serve as capture centres for free nonequilibrium electrons and the already present form O^- captures vacancies. In view of the condition of electroneutrality, transition to the ionogen form will be accompanied by formation of an equivalent amount of Ni^{3+} ions. These processes lead to a modification of the amount of free charge carriers in the lattice. In the active system, the equilibrium will be shifted towards the ionogen form of oxygen (strong adsorption) so that superstoichiometry of such an oxide will consist mainly of the ionogen oxygen. According to the electron theory⁷, shift of the Fermi level towards the conductivity band takes place, this leading to the decrease of the hydrogen adsorption with respect to donor character of this adsorption and to the decrease of the rate of reaction. Consequently, the active samples will have a longer induction period and lower rate of reduction (negative effect of activity) than equal inactive samples reduced under equal conditions. This is in qualitative accordance with results of the study of the Japanese authors⁴ quoted, who observed decrease of the rate of reduction of NiO irradiated by γ -rays, as compared with reduction of the same non-irradiated sample. Their original sample is superstoichiometric oxide, mostly with neutral form of superstoichiometric oxygen, whereas the same sample irradiated, being reduced more slowly, is an oxide with predominantly ionogen form of superstoichiometric oxygen.

The observed increase of the rate of reduction of the active samples in the reduction immediately started after a preliminary heat treatment (Fig. 4) may be, therefore, interpreted as follows. The heat treatment results in the recovery processes, providing a temporary disappearance of practically all the defects raised by activity in the system. The strongly adsorbed ionogen form of superstoichiometric oxygen is again converted to a weak neutral form. The electrons pass over from the acceptor oxygen level to the valence band, or recombine by capturing a positive hole from this band. Degree of filling up the localized level thus decreases and equilibrium between both

forms is shifted towards a milder form. In the subsequent reduction, "normal" superstoichiometric oxide (with mostly neutral form of superstoichiometric oxygen) is then reduced at a higher rate already. This is in accordance with results of the study of the reduction of nickel oxide of various stoichiometry⁵ as well as with the results presented in paper², where it has been further shown that unlike pure nickel oxide the ionogen form of superstoichiometric oxygen of nickel oxide cannot be for the mixed NiO-ZnO system determined iodometrically⁹. The quantitatively undefinable reduction of zinc oxide, which changes with composition of the samples and temperature, does not allow with this system either thermogravimetric determination¹⁰ of all the forms of superstoichiometric oxygen present.

The heat treatment with a time delay before the subsequent reduction (first series of the experiments) is practically without effect on the kinetics of reduction of active samples in comparison with the inactive ones. In agreement with the literature data^{11,12} as well as with experimental results, a cumulation of the effect of activity in time cannot be assumed so that after the end of the treatment the original equilibrium state is attained within a short time in the system steadily irradiated by the incorporated radionuclide, and under these conditions effect of the treatment does not become evident. The increase of the rate of reduction and activation energy, observed for inactive as well as active samples treated at higher temperatures (500°C) is probably connected with uncovering new centres, with desorption of last traces of water which is always present in systems with superstoichiometric nickel oxide¹³. This factor was developed in paper² in a more detail.

The effect of the activity itself of the system (Table III) will take place already at lower values of the specific activity, when sample A is reduced considerably more slowly with high activation energy than an inactive sample of equal composition. Unlike this, reduction of sample B which has the specific activity by one order of magnitude higher than other samples, proceeds at a high rate with lower activation energy. It is then probable that with the increasing specific activity, inversion of the effect of radiation of the incorporated radionuclide upon the kinetics of the reaction studied takes place and the negative effect (slow-down of the rate) changes into the positive one. This gives proof primarily of the complex effect of the radiation itself of the system, and of the determining function of various mechanisms and effects as dependent upon specific activity, whereas magnitude of individual contributions cannot be quantitatively estimated. Analogous phenomena in the study of some catalytic reactions on solid active catalysts have been described in the literature¹². The ⁶⁵Zn radionuclide is from 1.5% a positron radiator. The emission of positively charged particles may result in the formation of a negative charge localized on the solid phase surface. Owing to the donor character of the hydrogen sorption (transfer electrons from substrate into the solid phase), a decrease of the adsorption ability of the surface with respect to hydrogen, and slow-down of the reduction can be expected. On the basis of experimental results and analysis Spicyn and co-

workers^{12,14} showed that effect of the surface charge upon reactivity of the solid phase will take place for active catalysts primarily in the region of low specific activities and ceases to be decisive at higher activities. Unlike this, other¹⁵ authors do not consider the charge localized on the surface as factor affecting the reaction rate at all.

In the region of higher specific activities, rather formation of point defects in the lattice, which are generated if energy of interacting γ -radiation is at least 1 MeV^{16,17}, probably takes place. The energy transfer primarily proceeds *via* the Compton electrons or photoelectrons, a part of which raises multiple ionization of the cascade character and a minor part can share through elastic collisions with lattice atoms in the formation of point defects of the interstitial-vacancy type. From the point of view of the band model of solids, the formation of defects means production of localized donor or acceptor levels in the energy gap and effect upon position of the Fermi level, responsible for the concentration of free charge carriers and hence for the absorption properties. Life of the defects of this nature and their thermal stability is relatively short so that the point defects as well as those of the charge character, are destroyed with the increasing temperature, due to the recovery processes. With the steadily radiating active catalyst, however, the reaction temperature practically determines immediate state of the equilibrium position of the process, which can be illustrated in the following way: Formation of defects \rightleftharpoons Decay of defects. It follows from experimental results of other authors^{14,18} that effects, either positive or negative, raised by ionizing radiation could be for active catalysts observed up to temperatures of several hundreds °C within the study of various catalytic reactions, unlike equal systems irradiated by an external source of radiation of the same kind. Consequently, if the concentration of point defects is sufficiently high, these defects may directly become active reaction centres in which the reaction will proceed with another activation energy. At higher specific activities, inversion of the effect of the activity of the system may then take place and the reduction will proceed more rapidly with lower activation energy. With the increasing number of point defects the reduction is accelerated due to speeding-up crystallochemical changes and formation of metallic nuclei^{13,19}.

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Translated by J. Hejduk.