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PHYSICO-CHEMICAL PROPERTIES OF $CuO-Bi_2O_3$ MIXED OXIDES AND MODIFICATION OF THEIR HYDROGEN REDUCTION REACTIVITY BY IONIZING RADIATION

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Abstract

This paper describes a study on some physico-chemical properties of $CuO-Bi_2O_3$ mixed oxides of various composition and their reactivity during hydrogen reduction in the range 290–460°C. Depending on the composition, the changes in the morphology of the samples, their specific surface areas, phase composition of Bi_2O_3 as well as the change in the amount of chemisorbed surface oxygen (specific surface oxidation ability) were found. The last mentioned parameter is strongly affected positively or negatively (depending on the dose absorbed) by the pre-irradiation with gamma-rays and accelerated electrons. Either reduction of CuO or consecutive reduction of both components with a maximum rate on the surface or sub-surface layers of grain, proceed in different temperature ranges.

The retarding effect of liquid bismuth is partially compensated for by the sponging and trapping effects, so that the overall reduction rate changes non-monotonously with the composition of the samples. Pre-irradiation leads in all cases to the lowering of reduction rate, which can be correlated with the increase in the concentration of strongly bound oxygen forms, creating centres of donor hydrogen chemisorption. The effect of gamma-radiation appears to be function of the threshold dose absorbed.

Keywords: $CuO-Bi_2O_3$ mixed oxides, ionizing radiation, physico-chemical properties

Introduction

The properties of Bi_2O_3 have been studied by many authors predominantly from the catalytic point of view [1, 2]. In mixture with MoO_3 bismuth(III)oxide enhances both the activity and selectivity of catalysts (bismuth molybdates) in the partial oxidation of alkenes [3]. Relatively little attention has been paid to the reactivity of Bi_2O_3 during its reduction by gaseous reducing agents, in which, depending on the reduction temperature, liquid phase metallic bismuth

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is formed. Similarly as in other oxides of low-melting metals [4, 5] the pronounced influence on the reduction behaviour of Bi_2O_3 by admixtures of foreign oxides likewise undergoing reduction can be expected.

Changes in reactivity of some pure oxides or multicomponent oxide systems during their hydrogen reduction can also be induced by various sorts of ionizing radiation, but only at appropriate doses absorbed [6, 7]. From this point of view only few literature data relating to the radiation sensitivity of the systems containing oxides of low-melting or volatile metals, are available. Accordingly our effort was concentrated on the study of the basic physico-chemical properties of $CuO-Bi_2O_3$ mixed oxides differing in composition. The hydrogen reduction kinetics of this system and its modification by pre-irradiation with gamma-rays and accelerated electrons have also been investigated.

Experimental

Oxide mixtures of varying composition in the range 0–100 wt.% were prepared by thermal decomposition of the precursors (basic carbonates of both metals) for 3 h at 600°C in air. The starting solution of bismuth nitrate of 1 $mol \cdot l^{-1}$ concentration was obtained by heating an aqueous suspension of basic bismuth nitrate $4BiNO_3(OH)_2BiO(OH)$ with an admixture of HNO_3. After filtering, the solution was mixed with a 1 $mol \cdot l^{-1}$ solution of AR grade $Cu(NO_3)_2 \cdot 6H_2O$ in the required ratios of both metals. The precipitation was performed with a 10% stoichiometric excess of aqueous Na_2CO_3 solution of 2 $mol \cdot l^{-1}$ concentration under vigourous agitation at 40°C. The precipitates were carefully washed, dried at 160°C and homogenized by grinding in an agate mortar. The optimum conditions of decomposition were first established by DTA measurement of the selected precursors differing in composition.

The content of metals in the mixed oxides was determined by atomic absorption spectroscopy. The qualitative phase composition of the samples was investigated by X-ray diffraction using a TUR M 62 generator with a goniometer. Nickel-filtered CuK_α-radiation was used. Specific surface areas were measured by low temperature selective adsorption of nitrogen from an N_2/H_2 mixture and the morphology of the samples was studied using a JSM 50A (Jeol) scanning electron microscope. The content of ionogenic chemisorbed oxygen was determined by iodometric titration according to [8]. The standard DTA measurement was performed on a Netzsch STA 409 thermoanalyser within the range 20–900°C at a heating rate of 10 $deg \cdot min^{-1}$.

The samples were divided into several fractions. The first and second portions were irradiated with ^{60}Co γ-rays in air at doses of 1,5 MGy and 3 ± 0.1 MGy, the third portion was irradiated at a dose of 600 kGy by accelerated electrons with an average energy of 4 MeV from a high frequency linear accelerator. The reduction kinetics was studied by isothermal thermogravimetry in the range 290–460°C under identical conditions for all the original and pre-irradiated mixed oxides. Conditions were used in which the rate of reduction was independent of the flow rate of hydrogen for any sample composition. This was ensured at a flow rate of 56 $ml\cdot min^{-1}$ and a standard weight of sample 50 mg was used in all experiments.

Results and discussion

Basic physico-chemical properties of CuO–Bi_2O_3 mixed oxides

As it follows from the results of chemical and phase analysis (Table 1), the thermal decomposition of the precursors under given conditions leads to a product the major components of which are the oxides of stoichiometry CuO and Bi_2O_3. In the region of a high excess of copper the successive desorption of the water up to 200°C takes place during the decomposition of the starting basic

Table 1 Chemical and phase composition of CuO–Bi_2O_3 mixed oxides and their specific surface areas (S)

Sample	Chemical composition / wt %			Phase	S /
	CuO	Bi_2O_3	$CuO+Bi_2O_3$	analysis	$m^2\cdot g^{-1}$
1	97.98	0.00	97.98	only CuO	7.3
2	96.49	3.01	99.50	Cu O, slightly γ–Bi_2O_3	4.9
3	89.94	7.49	97.43	Cu O, slightly γ–Bi_2O_3	5.8
4	88.31	9.43	97.65	Cu O, γ–Bi_2O_3, slightly α–Bi_2O_3	4.2
5	81.94	15.68	97.62	Cu O, γ–Bi_2O_3, 1.6 content of α–Bi_2O_3 increases	2.0
6	76.06	22.78	98.89		
7	60.89	53.51	98.46		1.3
8	53.26	43.87	97.13		0.9
9	45.81	53.44	99.25		1.3
10	30.16	67.87	98.03	slightly CuO, max. conc. of α–Bi_2O_3 and γ–Bi_2O_3	1.4
11	19.51	77.52	97.03		0.9
12	16.56	81.46	98.02	γ–Bi_2O_3, slightly α–Bi_2O_3	0.8
13	4.39	93.27	97.66	β–Bi_2O_3 , γ–Bi_2O_3, very slightly α–Bi_2O_3	1.4
14	3.20	94.93	98.13		1.3
15	0.00	98.40	98.40	β–Bi_2O_3, very slightly γ–, α–Bi_2O_3	0.9

copper carbonate, so that the thermogravimetric curve shows only a small weight loss (Fig. 1, curve TG-A).

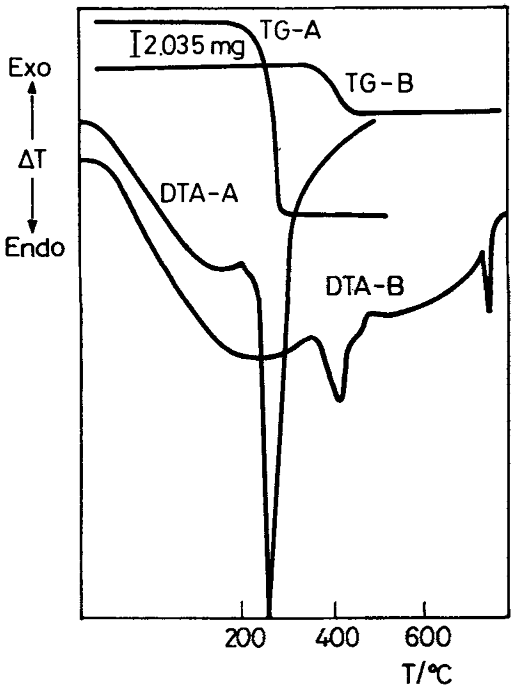

Fig. 1 DTA and TG curves of the precursors (mixed basic carbonates) corresponding to samples No. 1 (A) and 15 (B)

The pronounced endothermal effect in the DTA curve at 280°C corresponds to the simultaneous dehydroxylation and release of CO_2 at complete transformation to the final copper(II)oxide. On the second edge of the series the decomposition of bismutite $(BiO)_2 \cdot CO_3 \cdot H_2O$ is characterized by an endothermic peak at about 430°C (loss of molecular water and CO_2) likewise after the previous release of the water adsorbed (Fig. 1, curves B). The following endothermal effect at 730°C represents the phase transformation of α-γ–Bi_2O_3 to the δ–modification in the final product. For the mixed precursors the TG-curves show in the region of 280–390°C a stepwise increase in weight-loss corresponding to the dehydration of bismutite, and the slight DTA-endothermal effect at 430°C represents, in contrast to the pure precursor, only the loss of CO_2. Accordingly, two consecutive processes yielding the final two-component oxide system take place. According to some literature data, the DTA curves of pure anhydrous bismutite show the only endothermal effect at 490°C [9] and the pure basic copper carbonates (malachite, azurite) are characterized also by an endothermic peak at about 400°C [10]. Our results concerning the decomposition of basic copper carbonate are in accordance with those recently obtained by simultaneous measurement of ETA-TG-DTA curves [11].

It is evident from Table 1 that bismuth(III)oxide is present in mixed system in all phases, at the beginning of the series predominantly as $\gamma-Bi_2O_3$ and with decreasing content of CuO the amount of the α-phase increases reaching a maximum concentration for samples 9–11. In the region with the highest content of Bi_2O_3 its β-phase with tetragonal lattice prevails and the amount of γ- and $\alpha-Bi_2O_3$ decreases. The presence of additional selective reflections in a broad region of composition from 80 to 20 wt.% of CuO, probably corresponding to the binary compounds of both oxides with unidentified stoichiometry, provides evidence for the strong mutual interaction in the system under study. The low values of specific surface area can be attributed to the relatively high calcination temperature of the precursors (600°C) and sintering processes. With increasing content of Bi_2O_3 up to 20 wt.% the magnitude of this parameter decreases and then it does not change (Table 1). It follows from the morphological investigation of the samples that the particles are created as agglomerates with average size of about 5 μm (Fig. 2) without distinct porous texture.

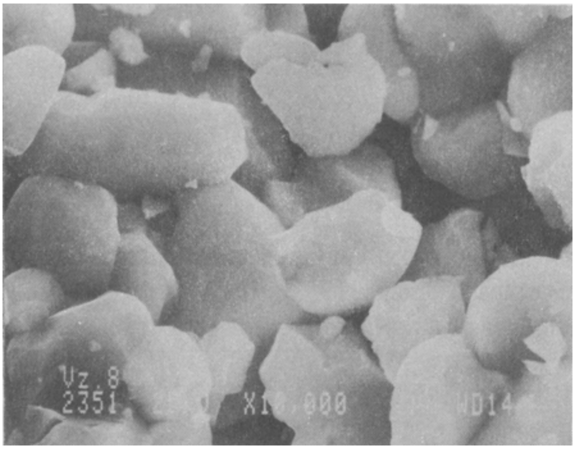

Fig. 2 Electron micrograph of the original sample No. 8, magnification 10^4x

Similarly as in other oxide systems [7, 12] the applied ionizing radiation in the dose range used causes no changes in the physico-chemical parameters except the content of ionogenic chemisorbed oxygen (oxidizing ability of the surface).

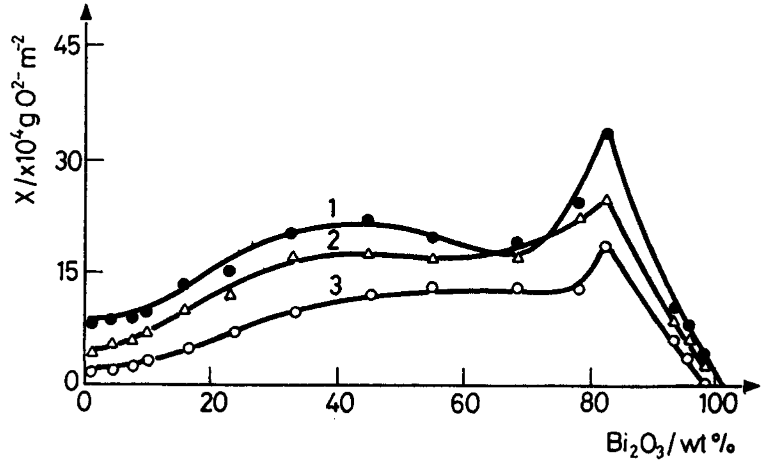

Fig. 3 Effect of pre-irradiation on the content of ionogenic oxygen for samples of various compositions expressed by the quantity ΔX (%); 1 – gamma, dose 3,0 MGy; 2 – accelerated electrons, dose 0,6 MGy; 3 – gamma, dose 1,5 MGy

The dependence of this parameter normalized to unite surface area on the composition and age of the samples is shown in Fig. 3. A maximum of the dependence in the region of an excess of Bi_2O_3 gives evidence for the fact that the dissociative chemisorption of molecular oxygen probably takes place not only on the majority centres formed by the pairs of lower valency ions of bismuth, but also on the additional mixed centres according to the following equation:

$$Cu^{+}\text{–}Bi^{2+} + O_2 \rightarrow Cu^{2+}\text{–}Bi^{3+} + O^{2-}$$

The presence of surface Cu^{+} ions in various concentrations depending on the composition, was also proved in other two-component systems $A^{II}O\text{–}B_2^{III}O_3$ (A = Cu) by ESCA measurement [13] similarly as the presence of the lower valency ions of bismuth including Bi^{2+} in the region of its excess [14]. The ageing of the samples manifests itself by changes of the dynamic equilibrium between surface and aerial oxygen i.e. by the alteration of the absolute amount of superstoichiometric oxygen at practically unchanged character of the dependence on composition. In contrast to cupric oxide and mixed samples the freshly prepared pure Bi_2O_3 showed a non-measurable content of surface oxygen and its increment during the storage was also negligible. Analogously, the thermal treatment of the samples for 1 h at 400°C in various atmosphere (nitrogen and oxygen) followed by cooling to ambient temperature in the same atmosphere before the oxygen determination did not lead to changes of this parameter with pure Bi_2O_3. Similar behaviour was found with *p*-semiconductive nickel oxide containing only a small amount of superstoichiometric oxygen [7]. Bismuth(III)oxide shows the same type of semiconductivity under standard conditions, whereas at higher temperatures ($T > 500$°C) or lower pressures it converts to the *n*-type owing to the loss of oxygen [2]. The increase of the content of superstoichiometric oxygen (its ionogenic forms) with increasing content of cupric oxide, reaching about 80%, was found to be independent of the atmosphere used. This effect can be probably attributed to the diffusion of interstitial oxygen of copper(II)oxide from the bulk to the surface. According to [15] the diffusion of O^- ions begins earlier than the diffusion of neutral oxygen. After reaching Cu^{2+} ions on the surface, part of the O^- ions may yield a hole, forming Cu^{3+} ions. The following transfer of the neutral form of oxygen O° is connected with its transformation on the created centres Cu^{3+}–O^{2-} to the detectable ionogenic form according to the scheme

$$2Cu^{3+}\text{–}2O^{2-} + O^\circ \rightarrow 2Cu^{3+}\text{–}2O^- + O^{2-}$$

This may be the cause of the observed increase in the oxygen content.

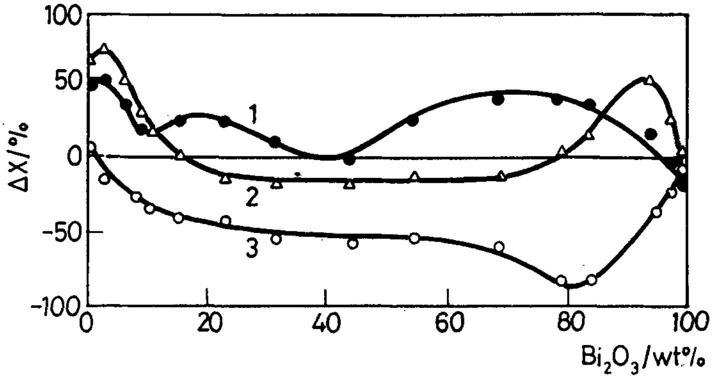

Fig. 4 Content of the superstoichiometric oxygen normalized to unit surface area X (g $O^{2-}\cdot m^{-2}$) *vs.* composition; 1 – samples after 5 months of storage; 2 – samples after 12 months of storage; 3 – freshly prepared samples

The influence of the ionizing pre-irradiation applied on the oxidizing ability of the surface, expressed by the quantity ΔX is shown in Fig. 4. This quantity is defined by the relation $\Delta X(\%) = 100(X^+ - X)/X$, where X^+ is the normalized content of ionogenic oxygen of the irradiated sample and X is the same quantity for the initial sample. As it follows from these non-monotonous dependencies of ΔX on composition, the prior gamma-irradiation with a lower dose leads to a negative effect ($\Delta X < 0$) in the whole range of compositions excluding pure cupric oxide, as a result of radiation reduction caused by the capturing of non-equilibrium electrons on the higher valency ions of both metals. Their charge is counterbalanced by the ionogenic oxygen, so that its content is lowered. A maximum of the negative effect lies at about 80 wt.% of Bi_2O_3 where the non-irradiated samples show the highest content of oxygen (Fig. 3). In accordance with earlier results [16] the dose of 1,5 MGy applied lies below the threshold value of radiation-induced changes of this parameter with pure copper(II)oxide. A slight negative effect leading to a small decrease in the amount of ionogenic oxygen with the older samples of pure bismuth(III) oxide was observed in all cases of pre-irradiation. Irradiation with accelerated electrons manifests itself, on the contrary, by a positive effect, the magnitude of which lies outside the limits of experimental errors (±15%) only in both marginal regions of the series including pure cupric oxide. Primary or ionization-generated electrons probably interact predominantly with a neutral, weakly bound form of oxygen which yields an increase in the concentration of ionogenic, strongly bound forms:

$$O^0_{2\,(ads)} + 2e^- \rightarrow O^{2-}_{2\,(ads)}$$

A similar effect was observed after γ-irradiation with a higher dose. Owing to the high density of Compton and photoelectrons with the greater part of samples oxidation takes place.

Kinetics of hydrogen reduction and the effect of pre-irradiation

At the lowest temperature (290°C) only the first nine samples with an excess of CuO are reduced at a measurable rate, whereas the reduction of all samples including pure, freshly prepared Bi_2O_3, proceeds at 380°C. It follows from the comparison of maximum weight-losses (degrees of reduction) with the theoretical values calculated assuming either total reduction of CuO or total reduction of both components that up to 350°C in the mixed system only cupric oxide is reduced and its degree of reduction decreases with increasing content of the second component. The reaction interface is mechanically blocked by the accumulating Bi_2O_3 which acts as an "inactive" admixture, so that the reduction of CuO in the deeper layers of grains entirely ceases. In the temperature range 380–430°C both components of the system are reduced. With increasing temperature the total degree of reduction (α_{total}) increases, but contrasting with pure cupric oxide the total reduction of mixed system is never achieved. With these samples the reaction interface is blocked by the product of bismuth(III)oxide reduction i.e. by a liquid phase of elemental bismuth. Its influence is especially evident at 460°C when the quantity α_{total} shows a lower value with the samples containing an excess of Bi_2O_3 including pure oxide than that at lower reduction temperatures. Analogous conclusions can be accepted for the one year old mixed samples, the reduction of which was followed under the same conditions. The effect of ageing and recrystallization manifests itself by the additional low-

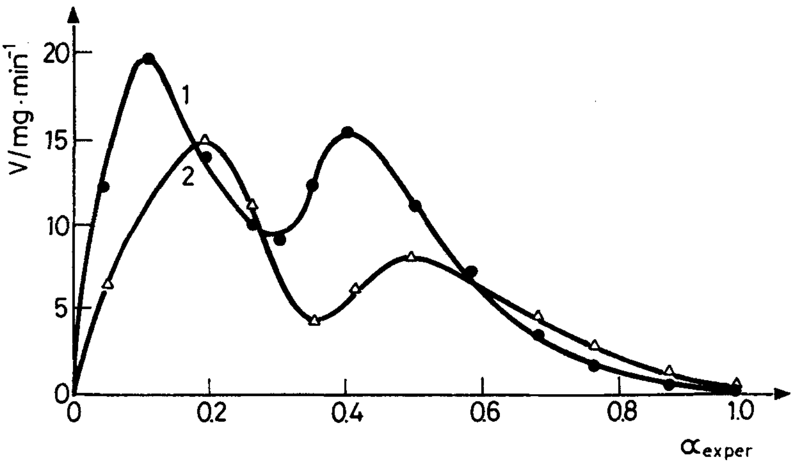

Fig. 5 Dependence of the specific maximum reduction rate $V_{s,max.}$ ($g^2 \cdot min^{-1} \cdot m^{-2}$) on the composition; 1 – reduction temperature 430°C; 2 – reduction temperature 380°C

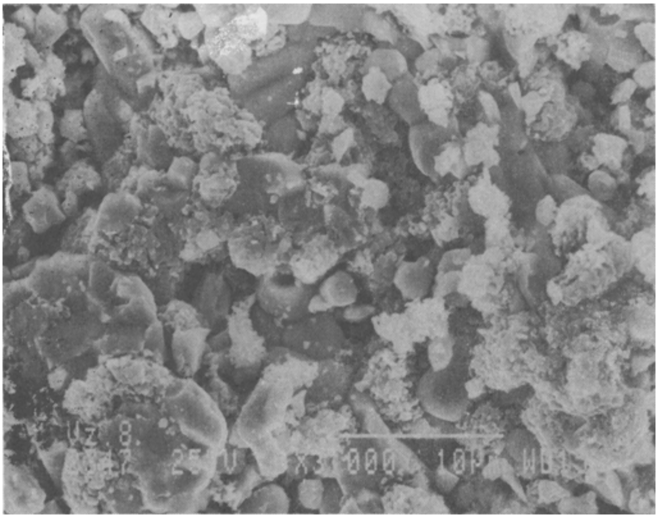

Fig. 6 Electron micrograph of the partially reduced sample No. 8, magnification $3 \cdot 10^3$×

ering of the quantity α_{total} and the rate of reduction. It follows from the analysis of the experimental weight-losses that the decrease in reactivity is much more pronounced with Bi_2O_3 as compared with cupric oxide.

The character of the kinetic curves of reduction changes with the composition of the system. With samples containing an excess of CuO the sigmoidal

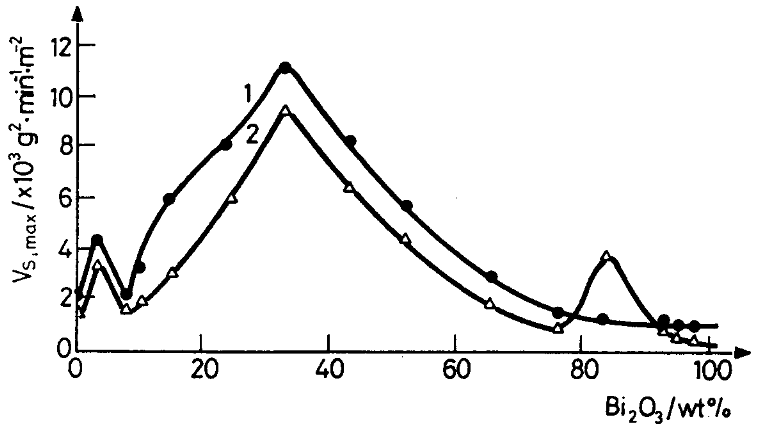

Fig. 7 Plot of instantaneous reduction rate V (mg·min^{-1}) *vs.* reduction degree $\alpha_{exper.}$; 1 – samples No. 11 reduced at 460°C; 2 – sample No. 14 reduced at 430°C

shape of the curves gives evidence of the nucleation control of a reaction whereas the reduction of mixed oxides with an excess of Bi_2O_3 proceeds with a maximum starting rate on the whole surface of the grain. The dependence of the instantaneous reduction rate on the reduction degree α (Fig. 5) for samples containing an excess of Bi_2O_3 and at higher temperatures shows two pronounced maxima followed by a continuous decrease in the reduction rate. From the given course and with regard to the different thermodynamic stability of both oxides it can be deduced that the reduction of the system under study proceeds in two consecutive, partially overlapping steps. The major part of cupric oxide is reduced preferentially and the nucleation as well as the first stage of agglomeration of the product are influenced by the presence of second component (Fig. 6). In the following stage the rapid surface reduction of Bi_2O_3 takes place and after creation of the transport barrier by the layer of liquid bismuth on the grain surface the reduction rate decreases.

For the quantitative description of the reduction kinetics of the mixed oxides studied partly the modified Prout-Tompkins equation [17], partly the Ginstling-Bronstein equation assuming the spherical diffusion as a rate-determining step were used. In the former case the congruence of the experimental results with the model was obtained over a wide range of the degree of reduction α = 0,1–0,8 only with samples containing the highest amount of CuO, in the latter case the model satisfied for the middle and final stages of reduction of mixed oxides with a high content of Bi_2O_3. This fact gives also evidence for the change of the reduction mechanism and of the rate-determining step with the composition of the samples. Since the reduction proceeds in all cases at maximum rate in the surface and near-surface grain layers, the reduction was characterized by the maximum rate normalized to unit surface area. The dependence of this specific maximum rate ($V_{s,\,max.}$) on composition shows a non-monotonic course (Fig. 7). It can be seen from this figure that a 20 wt.% admixture of CuO leads to the acceleration of Bi_2O_3 reduction which may be caused by the sponging effect i.e. the elemental liquid bismuth is partially bonded with the reduced copper by capillary imbibition. The continuous liquid layer retarding the interface reaction is in this manner broken. The same effect was proved during the reduction of various oxides of low-melting metals reduced in the presence of easily reducible admixtures like NiO, CuO etc. [19]. At higher reduction temperatures the reduction degree of Bi_2O_3 increases so that the product cannot be removed in sufficient amount, hence the local maximum at 80 wt.% of Bi_2O_3 diminishes.

On the second edge of the series in the region with an excess of cupric oxide its reduction is also accelerated by a small admixture of Bi_2O_3. Because this rate maximum remains unchanged at all temperatures when either CuO or both oxides are reduced, the positive effect can be connected with the presence of the original bismuth(III)oxide and the product of its reduction. In both cases the stage of nucleation and growth of nuclei by the destruction of a continuous layer of reduced copper can be facilitated. Moreover, owing to the strongly exothermic character of the cupric oxide reduction and a local overheating [16], the presence of a second component in sufficient concentration can affect the heat transfer and activate the new surface centres. Both positive effects superimpose so that the mixed system is reduced with the highest rate at about 30 wt.% of Bi_2O_3. Different reactivity of bismuth(III)oxide depending on its phase composition in various samples of the series cannot be excluded either. The X-ray diffraction of reduced samples in the region of the rate maximum showed that bismuth dissolves in copper under formation of an alloy or intermetallic compound. The binding of the reduction product of the oxide which is more difficult to reduce, by the second component (trapping effect) leads also to the acceleration of the overall reduction rate.

A different character and thickness of the layer of the reduction products of both oxides are evident from the results of reoxidizing experiments. The samples after primary reduction were oxidized in an oxygen flow up to a constant degree and then reduced again at the same temperature and flow rate of the corresponding gas. A very rapid oxidation of a thin layer of liquid bismuth proceeded only with samples containing an excess of Bi_2O_3, whereas the oxidation of the products of primary reduction from the second edge of the series, created predominantly by the compact layer of metallic copper, proceeded distinctly more slowly. The rate of secondary reduction of reoxidized CuO was comparable with that of the primary process, whereas the reduction of reoxidized and recrystallized Bi_2O_3 was five times slower as compared with the primary reduction.

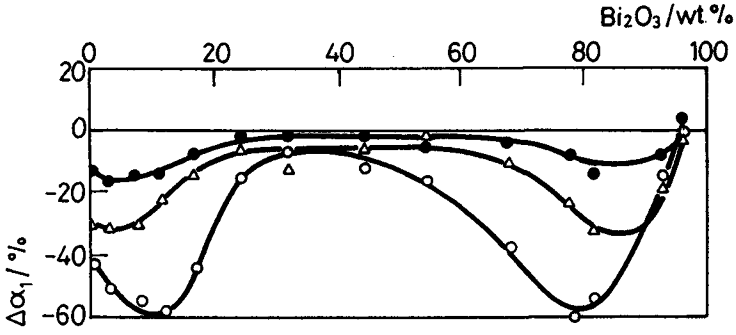

Fig. 8 Effect of pre-irradiation on the reduction kinetics of CuO–Bi_2O_3 mixed oxides, expressed by the quantity $\Delta\alpha_1$ (%); Reduction temperature 380°C; 1 gamma, dose 1.5 MGy; 2 accelerated electrons, dose 0.6 MGy; 3 gamma, dose 3.0 MGy

The effect of pre-irradiation on the reduction kinetics of mixed oxides at 380°C is demonstrated in Fig. 8 by the dependence of the quantity $\Delta\alpha_1$ (%) on composition. This quantity is defined analogously to ΔX, where X and X^+ are replaced by the reduction degrees achieved after one minute of measurable reduction course of the original sample α_1 and the same irradiation sample α_1^+. It is evident from the given dependencies that the system under study is most sensitive to the radiation applied in both marginal regions of the series up to about 20% admixture of the second minor component.

The radiation effect is in all cases zero for the pure bismuth(III)oxide, further for the mixed oxides in the region of 30 wt.% of Bi_2O_3 where the reduction rate of the original samples is highest (Fig. 7) and considering the total error of measurement (±15%), also in the whole range of compositions for samples irradiated with a lower dose of gamma radiation. This last finding is in accordance with the results of a previous more detailed study of the influence of dose (range from 1,4 to 14 MGy) on the reduction of γ–irradiated cupric oxides of various origin [16]. Positive effect has been found only at extremely high doses. Irradiation by accelerated electrons and a higher dose of gamma-rays in the present study leads, on the contrary, to a pronounced negative effect ($\Delta\alpha_1 < 0$) i. e. to a lowering of the reduction rate of mixed samples including pure cupric oxide. This effect is probably connected with the increase of the content of ionogenic, strongly bound oxygen (Fig. 4) in the same regions of composition as a result of the shift of equilibrium among the various surface oxygen forms [7]. Chemisorption of hydrogen, due to its donor character on the centres created by the ionogenic oxygen, is lowered and the reduction is therefore retarded.

The fact that in previous studies no similar correlation was found between the radiation influencing the reduction rate of CuO and changes of the content of ionogenic oxygen [16] follows from the different properties of cupric oxides (probably different ratio of various forms of surface oxygen) determined predominantly by the calcination temperature of the precursors ($T_{\text{calc.}}$ = 400°C) and the atmosphere used. The content of oxygen for the cupric oxide under study ($T_{\text{calc.}}$ = 600°C) is by an order magnitude higher and its lability is lower as compared with the oxides studied earlier. This is supported by the relatively slow and small changes of oxygen content with time (Fig. 3) in contrast to the cupric oxide of a "low-temperature origin" for which a 3-fold decrease in the oxygen content was observed already after twenty days of storage. The positive effects (acceleration of the reduction) induced by sufficiently high doses of γ–radiation, uninfluenced by the presence of strongly bound oxygen, can be attributed to the capture and stabilization of non-equilibrium electrons on the biographic lattice defects, leading to an increase in the reactivity of the interface in the course of crystallochemical transformation in the solid [13, 16].

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Zusammenfassung — Vorliegend wird eine Untersuchung der physikalisch-chemischen Eigenschaften von $CuO–Bi_2O_3$-Mischoxiden verschiedenster Zusammensetzung und deren Reaktivität bei der Wasserstoffreduktion im Temperaturbereich 290–460°C beschrieben. In Abhängigkeit von der Zusammensetzung, der Morphologie der Proben, deren spezifischer Oberfläche, der Phasenzusammensetzung von Bi_2O_3 und der Änderung des chemisch gebundenen Oberflächensauerstoffes. Der zuletzt erwähnte Parameter wird durch eine vorherige Bestrahlung mit Gammastrahlung und schnellen Elektronen stark positiv oder negativ (je nach adsorbierter Dosis) beeinflußt. In verschiedenen Temperaturintervallen verlaufen entweder die Reduktion von CuO

oder die konsekutive Reduktion beider Komponenten mit einer Höchstgeschwindigkeit an der Oberfläche oder in den unter der Oberfläche liegenden Strukturschichten.
Der Rückhalteeffekt von flüssigem Wismut wird teilweise durch die Bläh- und Fangeffekte ersetzt, so daß die resultierende Reduktionsgeschwindigkeit sich mit der Zusammensetzung der Proben nichtmonoton verändert. Eine vorangehende Bestrahlung führt in allen Fällen zu einer Verringerung der Reduktionsgeschwindigkeit, was durch die Entstehung von Zentren mit Donorwasserstoffchemisorption mit dem Ansteigen der Konzentration stark gebundener Sauerstofformen korreliert. Der Effekt der Gammastrahlung scheint eine Funktion der absorbierten Grenzschwellendosis zu sein.