

INFLUENCE OF COMPOSITION AND IONIZING RADIATION ON KINETICS OF REDUCTION OF MIXED CdO–ZnO OXIDES WITH HYDROGEN

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The reduction of cadmium oxide and zinc oxide mixtures of various compositions with hydrogen at 410–450° was studied with thermogravimetry. The reduction kinetics, which depends markedly on the composition in the whole composition range, can be described by the equation $(\alpha + 0.3)/(1 - \alpha) = A \cdot e^{kt}$. Preliminary irradiation of the samples with ^{60}Co γ -rays (applied dose $D_\gamma = 10^5$ Gy) causes an increase in the rate of reduction of samples containing an excess of CdO and decrease in the rate of reduction in the region with excess of non-reducible ZnO. Fast neutron irradiation with a flux density of $1.18 \cdot 10^{17}$ n/m² (total dose $D_n = 4.5 \cdot 10^2$ Gy) from a ^{252}Cf source retards the reduction in the whole range of composition. The probable mechanism of mutual interaction of both components and of the applied ionizing radiation is discussed.

Verhoeven and Delmon studied the hydrogen reduction of cadmium oxide [1] and other oxides of volatile metals [2]. They found that the small amounts of copper (2.8%) and nickel (3.2%) introduced by the decomposition of formates “in situ” do not affect the reduction of CdO. Pronounced changes in the kinetics of reduction of CdO have been found when In^{3+} (1.43 at. %), Li^+ (2 at. %) and Be^{2+} (0.74 at. %) are incorporated into its lattice [3]. In the two-component NiO–CdO system, the initial temperature of measurable reduction of CdO was lowered by about 150° in samples containing more than 24.85 mol. % NiO [4]. The kinetics of reduction of this system was markedly dependent on its composition. The reduction of pure oxides and multicomponent systems can also be influenced by various sorts of ionizing radiation [5, 6]. The resulting effect can be positive (acceleration of the reaction) or negative (a slowing-down), depending on the sort of radiation and the applied dose. We were therefore concerned with the reduction of the two-component system of ZnO and CdO under conditions when only one component is reduced.

Experimental

Preparation, analysis and physicochemical measurements

Oxide mixtures of varying composition were prepared by thermal decomposition of the mixed nitrates. Solutions of both nitrates (of reagent grade) in 1 M concentration were mixed in the required ratios, evaporated to dryness on a water bath

and heated in an electric furnace in the air, first for 1 h at 200° and then for 3 h at 400°. The product was ground and the fraction with grain size 0.05–0.165 mm was separated by sieving.

The contents of both metals were determined complexometrically, using selective precipitation of Cd with diethanoldithiocarbamate [7]. The specific surface area was measured by nitrogen adsorption at low temperatures. The samples were examined by X-ray powder diffraction techniques (Debye-Scherrer), using a TUR M 62 generator (Zeiss) with a goniometer. Nickel-filtered Cu radiation was used ($\lambda = 1.54178 \text{ \AA}$). The extents of the coherent regions were calculated for the two oxides in the system from the diffraction line half-widths. The morphology of the initial mixed oxides and of the reduced samples was investigated with JSM-50 scanning electron microscope (Jeol).

Irradiation

The samples were divided into several fractions. The first fraction was irradiated with ^{60}Co γ -rays at a dose of 10^5 Gy; the second was irradiated with fast neutrons in a commercial source of ^{252}Cf (Radiochemical Centre, Amersham) with a flux density of $1.18 \cdot 10^{17} \text{ n/m}^2$ (applied total dose $D_n = 4.5 \cdot 10^2$ Gy).

Apparatus and procedure

Reduction of the mixed oxides was followed in the temperature range 410–450°, under the same experimental conditions for the original oxides and for the samples subjected to preliminary irradiation. The reduction kinetics was studied with thermogravimetry in an apparatus described earlier [8]. Conditions were specified where the rate and time course of the reduction were independent of the flow rate of hydrogen for any sample composition (the sample weight was always 50 mg). This was ensured at the flow rate of $56 \text{ ml} \cdot \text{min}^{-1}$ used in all experiments.

Results and discussion

Physicochemical properties of mixed oxides

The compositions of the samples, their specific surface areas and the extents of the coherent regions are listed in Table 1. It follows from the analytical results that the experimental conditions used (temperature and time of decomposition) lead to the formation of mixed oxides of zinc and cadmium. The presence of cubic cadmium and hexagonal zinc oxides, with lattice parameters in good agreement with the tabulated values, was confirmed by microstructural analysis. IR-spectra showed the presence of trace amounts of water but no nitrate ions, and hence the decomposition was quantitative. Rather small specific surface areas varying within a range of two orders are typical for oxides prepared by the decomposition of nitrates [9]. This quantity generally increases with increasing cadmium oxide content and its non-additivity provides evidence of a higher degree of mutual interaction of the two

Table 1

Compositions, specific surface areas (S) and extents of coherent regions (L) of CdO-ZnO mixed oxides

Sample	Wt. %		S , m ² /g	L , nm	
	CdO	ZnO		CdO	ZnO
1	0.00	99.77	0.08	—	260.9
2	1.70	97.16	0.03	—	158.5
3	3.40	95.84	0.04	—	179.5
4	5.17	92.43	0.04	—	210.1
5	11.24	88.75	0.07	—	260.9
6	32.39	67.60	0.15	145.1	210.1
7	45.86	52.68	0.53	107.1	210.1
8	47.34	50.62	0.54	122.6	210.1
9	54.05	44.66	0.48	145.1	—
10	67.95	30.13	0.87	160.9	—
11	87.80	11.90	1.46	213.3	—
12	92.98	5.26	1.32	264.9	—
13	96.45	3.28	0.71	264.8	—
14	97.87	1.83	1.35	379.9	—
15	99.38	0.00	0.35	379.9	—

components than corresponds to a homogeneous mechanical mixture. Analogously, the extent of the coherent regions increases with increasing CdO content for samples containing an excess of CdO, whereas the dispersity of ZnO crystallites is practically independent of the composition. In contrast to other two-component heterophase mixed oxides [10], the specific surface areas are not directly correlated with the size of the crystallites. Study of the sample morphology reveals that the surface area is determined by the geometry and porosity of the larger agglomerates, i.e. by the grain size, which similarly changes within a range of two orders, depending on the composition. For the doses used, neither the specific surface areas nor the structures of the samples changed.

From the point of view of the semiconducting properties, both oxides are n -semiconductors; with CdO the excess of Cd²⁺ ions is attained by vacancies in the oxygen sublattice, whereas with ZnO the superstoichiometry of the metal ions is due to the interstitial ions Zn⁺ and Zn²⁺, their ratio being dependent on the temperature [11]. In accordance with the mentioned character, no presence of ionogenic chemisorbed oxygen was found by iodometry [12], either for the original oxides or for irradiated samples, in the whole range of composition.

Kinetics of hydrogen reduction

The experimental results indicate that, in agreement with the thermodynamic properties of both oxides, under the given conditions CdO is the only reducible component in the system. At the lowest temperature applied, 410°, the reaction

proceeded at a measurable rate only with pure CdO (sample 15) and with mixed oxides containing more than 3.4 mol. % CdO. Consequently, in all cases the reduction was followed above the melting point of cadmium (320.9°), whose vapour tension at this temperature is considerable.

Figure 1 shows the dependence of the rates of instantaneous reduction of pure CdO and mixed oxide on the reduction degree α , defined as $\alpha = \frac{G_t}{G_{\max}}$, where G_t is the experimental weight loss in time t , and G_{\max} is the theoretical weight loss corresponding to the total reduction of CdO in the sample of given composition.

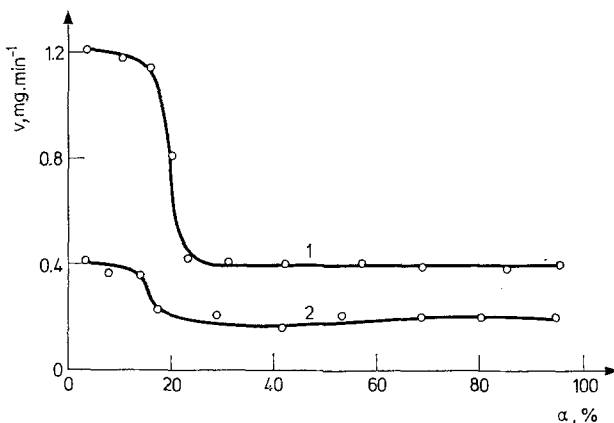


Fig. 1. Dependence of V ($\text{mg} \cdot \text{min}^{-1}$) on the reduction degree α (%). (1) sample 15 reduced at 435°; (2) sample 8 reduced at 410°

It can be seen from this Figure that the reduction proceeds after the latency period with the maximum initial rate up to $\alpha \sim 15-20\%$, but the rate then drops rapidly to a constant value. The mentioned course, typical for all the samples, is in accordance with the non-sigmoid character of the time vs. conversion curves and has also been found by other authors [1-3]. From the time courses of the reduction at different temperatures and from a comparison of the dependence of the maximum reduction rate on the composition at different temperatures, it follows that neither the evaporation of the reduced cadmium, as a consecutive process, nor its aggregation state [1, 4] influence the initial phase of the reduction. The constant rate interval (Fig. 1) demonstrates in contrast that at higher values of α and higher temperatures the reduction rate is determined by the evaporation of cadmium. The length of the latency period, which is independent of the composition, is a pronounced function of the reduction temperature.

The reduction kinetics for the studied samples can be described quantitatively by the equation $(\alpha + 0.3)/(1 - \alpha) = A \cdot \exp(kt)$, where α is the degree of reduction at time t , and A and k are constants. From the slope of the initial linear section of the dependence $\log(\alpha + 0.3)/(1 - \alpha) = f(t)$, corresponding to the presence of

liquid cadmium, the rate constants were calculated. From their dependence on the composition (Fig. 2) it is apparent that the rate of reduction generally increases with increasing content of the non-reducible component. The increase in this quantity is more marked at higher reduction temperatures. The dependence of the apparent activation energy of reduction on the composition exhibits a trend that can be correlated with that for the dependence of the rate constants, e.g. the activation energy decreases with increasing ZnO content. In contrast to the earlier-studied system CdO–NiO [4], where analogous dependences of the rate constants k and of the maximum reduction rate (V_{\max}) on the composition were found, for the CdO–ZnO system the value of V_{\max} increases with increasing CdO content (Fig. 2).

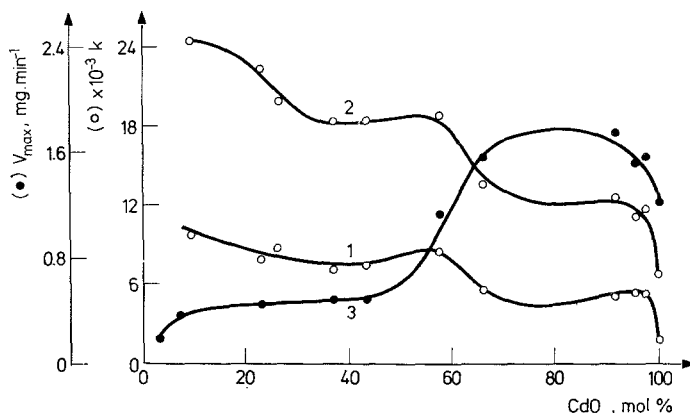


Fig. 2. Dependence of k (in relative units) and of V_{\max} ($\text{mg} \cdot \text{min}^{-1}$) on the composition. (1, 2) k , reduction temperatures 410 and 435°; (3) V_{\max} , reduction temperature 435°

From the mentioned dependences and from other experimental results, it can be deduced that the rate-determining step is not the adsorption of hydrogen as in the former case (CdO–NiO); the governing factors are only the reactivity and the rate of interphase metal-oxide progress, controlled by the rate of radial growth of the nuclei. At higher temperatures the reaction begins practically simultaneously on the greater number of surface centers, so that a continuous reaction zone is rapidly formed. The reduction rate is then drastically lowered (Fig. 1) owing to the covering of the whole surface with a layer of liquid, reduced cadmium. Since the liquid metal also covers the grain surface of the ZnO (Fig. 3), with the increase of the content the retarding effect of the reduction product diminishes and the total reduction rate increases. From this point of view the studied system can be conceived particularly in the region of a high excess of ZnO, as an active component (reducible CdO) in interaction with an inactive carrier (non-reducible ZnO). This acts as a stabilizing factor, which raises the dispersity of the CdO, and facilitates transport of the reducing gas and evaporation of the metal, so that the reaction proceeds on the “pure” surface of CdO. On the other hand, the value of V_{\max} measured in the initial stage of the process decreases with increasing ZnO content, owing to the blocking of

active sites on the reactive interphase by the non-reducible component (Fig. 2). This course is typical for the reduction of two-component oxides containing only one reducible component [13]. In the region of the center of the series, the equilibrium of the two counteracting effects can be assumed, and hence V_{\max} is practically independent of the composition.

The determining role of the area and reactivity of the interphase also follows from the experimentally found correlation between the specific surfaces and the maximum reduction rate. The heat treatment of samples in air in the temperature interval 500–650° for 1 hour results in the lowering of the specific surfaces owing

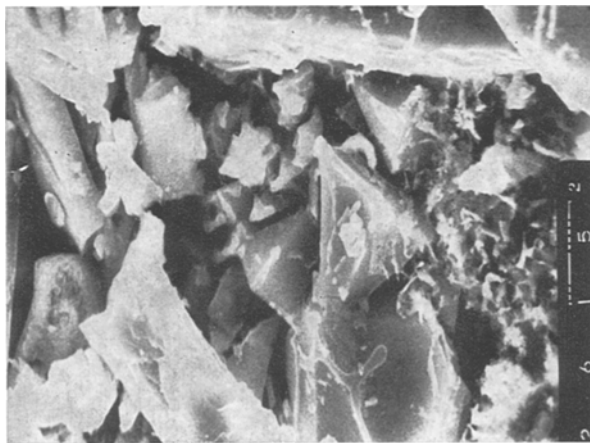


Fig. 3. Electron micrograph of partially reduced sample 5. Magnification $10^4 \times$; the line segment indicated corresponds to 2 μm

to sintering (the mean value of this lowering amounts to 30%) as well as in the partial release of oxygen from the CdO lattice, which are connected with the decrease in the reduction rate. Analogously with the changes in the specific surfaces, this is probably connected with the lowering of the rate of the secondary reduction. In these experiments, after the primary reduction at 410° the samples were oxidized in air stream to a constant degree and secondarily reduced with hydrogen at the same temperature. In addition to the decrease of the reduction rate, the overall character of the time vs. conversion curves was also changed. Examination of the morphology revealed that the liquid cadmium is oxidized by atmospheric oxygen, resulting in recrystallized CdO; this displays a different dispersity as compared with the initial sample. The fact that the admixture of powdered Pd (up to 1%) does not affect the kinetics of reduction of the initial samples provides further evidence that the adsorption of activated hydrogen and the pill-over effect are not the rate-controlling step.

Influence of ionizing radiation

The reduction of the irradiated samples was examined in the same temperature region as for the original mixed oxides 1–5 days after the end of irradiation. At 410°, only the samples containing more than 26 mol% CdO (after γ -irradiation), and at 450° only those containing more than 24 mol% CdO (after fast neutron irradiation) were reduced at a measurable rate. The effect of prior irradiation on the kinetics of the reduction is shown in Fig. 4 as the dependence of the quantity $\Delta k(\%) = 100[(k^+ - k)/k]$ on the composition, where k^+ is the rate constant of the reduction of the irradiated sample at the given temperature and k is the value pertaining to the initial oxide.

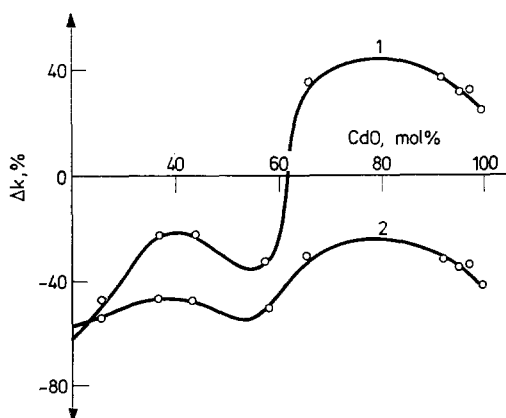
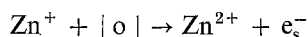


Fig. 4. Plot of magnitude Δk (%) vs. composition for samples irradiated with γ -rays (1), fast neutrons (2) and reduced at 435°

It can be seen that γ -irradiation results in a positive effect (increase of the reduction rate as well as of the value V_{\max}) in the region of a pronounced excess of CdO (more than 60 mol%), which converts to a negative one for the samples containing ZnO as the main component. In contrast, fast neutron irradiation leads to a lowering of the reduction rate in the whole composition range. With increasing temperature, the extents of both effects decrease, being about 50% lower at 450° than at 435°. From the presence of the temperature and time annealing processes it can be deduced that the changes in the reduction kinetics are connected with the radiation-induced defects, the stability of which depends on the reaction conditions.

The γ -irradiation leads primarily to the formation of non-equilibrium electrons by ionization processes which can be predominantly stabilized on the oxygen vacancies of the CdO lattice. Accordingly, the increase of their concentration, resulting in the enhancing of the reduction rate, appears to the highest extent in samples containing an excess of CdO. The enhanced reactivity of the interphase and the higher reduction rate are accompanied by a decrease in the apparent activation

energy of reduction by approximately 20%. With increasing ZnO content, the concentration of electrons decreases, probably due to the charge interaction of the two components in close contact. The interstitial Zn^{+} ions of ZnO interact with oxygen vacancies of CdO by the following process:



where $|o|$ is an oxygen vacancy an e_s^{-} is an electron stabilized on the vacancy. As a result, the positive effect of irradiation changes to a negative one. In the mentioned region the reduction proceeds with a high activation energy (on average 180 kJ/mol), which is practically independent of the composition of the mixed oxides. It follows from the non-monotonic dependence of the extent of the radiation-induced effect that the degree of mutual interaction of the two components, as well as the concentration of defects on the interphase, change with the composition, depending on the dispersity of the systems and the surface areas. Irradiation with fast neutrons can result in the formation of point defects of the lattice, and to a smaller extent in the formation of charge defects by secondary ionization processes. The increase in concentration of the oxygen vacancies in the CdO lattice accelerates its crystallochemical changes, due to the lattice deformation, as well as the rate of reduction. If ZnO is present, the concentration of vacancies is lowered by the above-mentioned interaction, so that the total rate of reduction is diminished. The fact that the rate of reduction of pure CdO also decreases after its neutron irradiation is evidence of another retarding process. The cause of the destruction of existing reactive centers (polishing effect of irradiation) may be a recrystallization process as a result of the local temperature increasing during the absorption of neutrons by cadmium, or of the presence of microconcentrations of new admixtures formed by the (n, γ) reaction of some cadmium isotopes.

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ZUSAMMENFASSUNG — Die Reduktion von CdO/ZnO-Mischoxiden verschiedener Zusammensetzung mit Wasserstoff bei 410—450 °C wurde thermogravimetrisch untersucht. Die deutlich von der Zusammensetzung abhängende Reduktionskinetik kann durch die Gleichung $(\alpha + 0.3)/(1 - \alpha) = A \cdot e^k$ beschrieben werden. Eine vorangehende Bestrahlung der Proben mit γ -Strahlen einer ^{60}Co -Quelle (angewandte Dosis: 10^5 Gy) verursacht eine Erhöhung der Reduktionsgeschwindigkeit bei Proben mit überschüssigem CdO und eine Verminderung der Geschwindigkeit im Bereich mit Überschuß an unreduzierbarem ZnO. Die Bestrahlung mit schnellen Neutronen einer ^{252}Cf -Quelle und einer Strahlendichte von $1.18 \cdot 10^{17}$ n/m² verzögert die Reduktion im ganzen Bereich der Zusammensetzung. Der wahrscheinliche Mechanismus der gegenseitigen Wechselwirkung beider Komponenten und der Einfluß der Bestrahlung auf die Reduktionskinetik werden diskutiert.

Резюме — Термогравиметрически при температурах 410—450° изучено восстановление водородом смешанных окислов CdO—ZnO различного состава. Кинетика реакции в значительной мере зависит от состава окислов и описывается уравнением $(\alpha \pm 0.3)/(1 - \alpha) = A \cdot e^{kt}$. Предварительное облучение образцов γ -лучами от ^{60}Co источника приводит к увеличению скорости восстановления образцов с избыточным содержанием CdO и к уменьшению скорости восстановления образцов с избыточным содержанием невосстанавливаемого ZnO. Облучение быстрыми нейтронами от источника ^{252}Cf с плотностью потока $1.18 \cdot 10^{17}$ н/м² замедляет восстановление во всей области состава окислов. Обсужден возможный механизм совместного взаимодействия обоих компонент и влияние облучения на кинетику реакции восстановления.