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REDUCTION OF CADMIUM OXIDE FROM (CdO + ZnO) MIXTURE

REDUKCJA TLENKU KADMU Z MIESZANINY (CdO + ZnO)

Reduction of cadmium oxide from (CdO + ZnO) mixture by means of a mixture of gases (CO + CO₂) and of carbon in the temperature range 1048—1200 K were investigated. It has been found that the reduction rate of CdO is proportional to the CO content in the mixture of the reducing gases. The effect of temperature and of the composition of the gaseous phase on the reduction rate of CdO and on the zinc content in the gaseous reduction products was determined. The value of the activation energy of this process has also been estimated. In the case of CdO reduction from zinc-cadmium carbonate by means of carbon the conditions were determined which should guarantee obtaining cadmium of Cd-“0” grade or cadmium oxide of „C” grade.

Przeprowadzono badania redukcji tlenku kadmu z mieszaniny (CdO + ZnO) za pomocą mieszaniny gazów (CO + CO₂) oraz węgla w zakresie temperatur 1048—1200 K. Stwierdzono, że szybkość redukcji CdO proporcjonalna jest do zawartości CO w mieszaninie gazów redukcyjnych. Określono wpływ temperatury i składu fazy gazowej na szybkość redukcji CdO oraz na zawartość cynku w gazowych produktach redukcji. Oszacowano także wartość energii aktywacji tego procesu. Przy redukcji CdO z węglanu cynkowo-kadmowego za pomocą węgla określono warunki, które winny zapewnić otrzymanie kadmu w gatunku Cd-„0” lub tlenku kadmu w gatunku „C”.

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1. Introduction

Obtaining of metals through the reduction of their oxides by means of carbon or CO belongs to the basic metallurgical processes. For this reason in the professional literature there can be found a number of studies referring to the reduction conditions of the compounds of these metals which are commonly applied by this method. Cadmium as a typical dispersed metal does not form isolated deposits, but it accompanies the zinc ores. For this reason the metallurgy of cadmium based mainly on processing various kinds of waste material and intermediate products of zinc industry, in which cadmium compounds concentrate. The raw material most often used to obtain cadmium is the so-called cadmium sponge, which is obtained in the cementation process of purifying ZnSO_4 solution before the process of electrolysis. It is contaminated mainly with zinc, and the preparation of metallic cadmium from this sponge is realized by the hydrometallurgical or by a combined method applying the distillation of cadmium in reducing atmosphere in order to obtain pure metal. Cadmium sponge can be also melted under a layer of salt, however this process causes great loss of the metal and is not widely applied.

Since the reduction process is not applied to obtain cadmium due to the lack of suitable raw material, the studies in this field have not found appropriate documentation in literature. If, however, a raw material with a high level of cadmium concentration could be obtained, it should be considered whether a method in which cadmium is obtained in the process of selective reduction would not be more profitable. Such a material might be the zinc-cadmium carbonate obtained in the processing of dust from blast roasting of zinc-lead concentrates on D-L machine. It contains about 10–15% of Zn and 40–45% of Cd.

Thermodynamic calculations of the equilibrium composition of the gaseous phase based on the discussion of Ptak and Sukiennik [1–2] for the reduction reaction of CdO and ZnO by means of a mixture of gases ($\text{CO} + \text{CO}_2$) and carbon, presented in the papers [3–5], show that the composition of the gaseous phase in the reduction zone will be within an area in which the reduction of zinc oxide be made impossible. Similar conclusions result from the analysis of the equilibrium composition of the gaseous phase with simultaneous occurrence of Boudouard's reaction. The problem is the more interesting that according to literature data [6], the reaction rate of the reduction of cadmium oxide by means of CO at the temperature 1273 K is about 200 times greater than the reaction rate of the reduction of zinc oxide. Moreover, from the values, presented in the study [7], it follows that the ratio of the reduction reaction rate to the rate of Boudouard's reaction is 10^3 for ZnO, whereas for CdO it is equal to 10^5 . This is evidence of the possibility of selecting such conditions which would ensure a selective course of the reduction process of CdO from the mixture ($\text{CdO} + \text{ZnO}$).

The aim of the study was to determine the conditions which will ensure a selective progress of the reduction process of CdO considering the zinc content in the obtained metallic cadmium.

2. Experimental results and their discussion

In order to realize the aim of the study the investigations were carried out in two variant forms. The first comprised the determination of the effect of the composition of the gaseous phase and temperature on the reduction rate of CdO from a mixture of oxides (CdO + ZnO) and on zinc content in cadmium. The investigations were conducted on material obtained from decomposition at the temperature 1073 K, of zinc-cadmium carbonate, of industrial production. It contained 49,95% of Cd and 16,8% of Zn. The second variant comprised the investigations of the reduction process of zinc-cadmium carbonate by means of carbon. In this variant the effect of temperature on the zinc content in metallic cadmium and in the obtained dust was determined.

The first variant was realized in a pipe electric furnace through which the gaseous phase in the amount of 45 dm³/h was passing. The amount of the flowing mixture of gases (CO + CO₂) was controlled and regulated by means of rotameters calibrated prior to the experiment. A definite mass of oxide material, in an alundum boat, was introduced into a furnace, heated to the preset temperature, through which a gaseous phase of a predetermined composition was passing. After a fixed time of reduction the material was taken out from the furnace, weighed and placed in the furnace again for some definite time. The process was stopped in the loss of the mass of the samples oscillated near the theoretical loss. In the conditions in which the measurements were carried out, on account of the small mass of the samples lack of proper conditions for condensation, the obtained dust contained partly oxidized cadmium vapours. The dust was collected jointly from the given measurement variant and subjected to chemical analysis for zinc content. The remainder of the process, of known mass, was subjected to chemical analysis for the content of cadmium. The results of the chemical analysis enabled to calculate the total degree of reduction of cadmium oxide and revealed the purity of the obtained product (in the form of metallic cadmium or cadmium oxide) in consideration of the presence of zinc.

The second variant of measurement comprised the reduction of zinc-cadmium carbonate by means of carbon, added in the amount of 10% in relation to the mass of carbonate. Experiments were conducted on samples with the mass of about 1000 g, by means of an apparatus consisting of a steel retort, above which the condenser was placed. After leaving the condenser the gases passed through an additional container the task of which was to catch the oxidized metal vapours. The scheme of the measuring apparatus has been presented in the study [3]. The process was stopped when any evolution of the gases was not observed, which was established on the basis of the combustion of the post-reduction gases.

The results of a relative change in the mass of the samples, subjected to reduction under various conditions, are given in Table 1. They show that the rate of changes of the mass depends in a higher degree on the composition of the gaseous phase than on the temperature of the process. It should be noted that considering the cadmium content in the examined samples and assuming the selective course of the reduction reaction, the maximal relative loss of the mass of the preparations should be equal to 52,5%. In the performed experiments, especially at higher temperatures of the

TABLE 1

Results of the investigations of the reduction of cadmium oxide from (CdO + ZnO) mixture by means of a mixture of gases (CO + CO₂) at various temperatures

Flow of the gaseous phase [dm ³ /h]		Reductions time [min]	Relative loss of the sample mass, [%]		
			Temperature of the process, [K]		
CO	CO ₂		1048	1073	1148
15	30	10	7.62	9.80	16.20
		20	16.80	18.70	25.30
		30	25.24	26.38	31.65
		45	35.18	35.26	40.30
		60	39.26	40.90	46.96
		90	45.62	47.88	52.23
		120	49.40	51.06	
22.5	22.5	10	12.70	16.12	19.80
		20	25.41	26.20	32.50
		30	34.38	36.55	40.20
		40	38.62	40.33	44.86
		60	44.06	46.40	51.24
		90	49.12	50.94	53.21
		120	51.19	52.40	
30	15	10	17.60	19.76	22.50
		20	32.30	33.40	38.20
		30	40.78	41.67	47.00
		40	45.20	46.30	50.60
		60	48.91	50.47	54.14
		90	51.75	51.92	54.72
		120	52.41		
45	0	5	13.40	14.37	16.09
		10	25.20	26.80	28.91
		15	33.80	34.89	38.60
		20	40.57	40.81	45.70
		25	44.40	45.30	48.96
		30	46.20	47.90	52.10
		40	48.51	52.69	54.20
		60	52.73	54.97	55.55
		90	54.16		56.88

process and higher CO concentration in the gaseous mixture ($\text{CO} + \text{CO}_2$), the relative loss of mass exceeded the maximal value. The question may be asked to what extent the zinc oxide participates in the reduction process. The main problem was if it would be possible, on the basis of the registered changes in the mass of the preparations, to determine the degree of CdO reduction, and further or to define the dependence of the changes in the rate reduction on the composition of the gaseous phase and temperature. In order to answer this question there have been carried out investigations of reduction at the temperature 1148 K by means of pure CO. During the measurement the loss of mass was registered, and at the same time the sample was subjected to chemical analysis for cadmium content. The results of these investigations are listed in Table 2. The obtained results show good agreement between the degree of CdO reduction, calculated according to chemical analysis and that calculated on the basis of changes in the mass up to the value of about 90%. Above this value the discrepancies between these values can be observed which is evidence of the occurrence of the process of ZnO reduction when the CdO content in the preparations was small. At lower temperatures and lower CO concentration in the gaseous mixture the reduction process should occur with higher selectivity.

TABLE 2

Relation between the degree of CdO reduction calculated according to chemical analysis and according to the relative change of mass at the temperature 1148 K

Relative change of mass, [%]	Cadmium content in remainder after reduction, [%]	Degree of CdO reduction, [%]	
		according to chemical analysis	calculated on the basis of mass changes
18.20	36.43	35.12	34.67
27.60	30.52	51.96	52.57
33.50	25.56	63.05	63.81
42.10	16.40	79.45	80.19
49.30	6.71	92.60	93.90
54.80	0.88	99.14	> 100

Basing on the obtained results (Table 2) there has been calculated, using the registered changes in the mass, the degree of CdO reduction, which is shown in Figs 1—3. The character of the obtained dependencies shows that a change in CO concentration in the mixture of the reducing gases ($\text{CO} + \text{CO}_2$) very strongly contributes to the increase of the rate of CdO reduction. The results obtained at various temperatures are evidence of a small influence of temperature on the reduction rate.

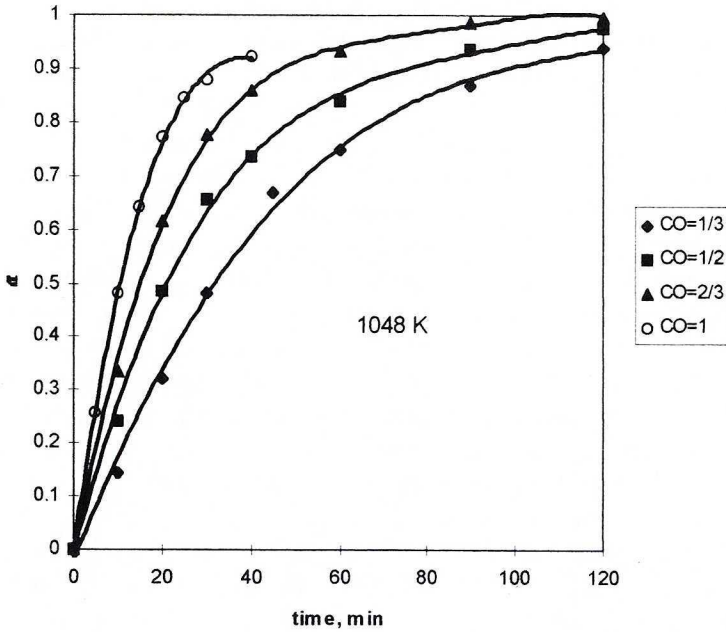


Fig. 1. Dependence of the degree of CdO reduction on the time of the process for various CO concentrations in the gaseous phase, at the temperature 1048 K

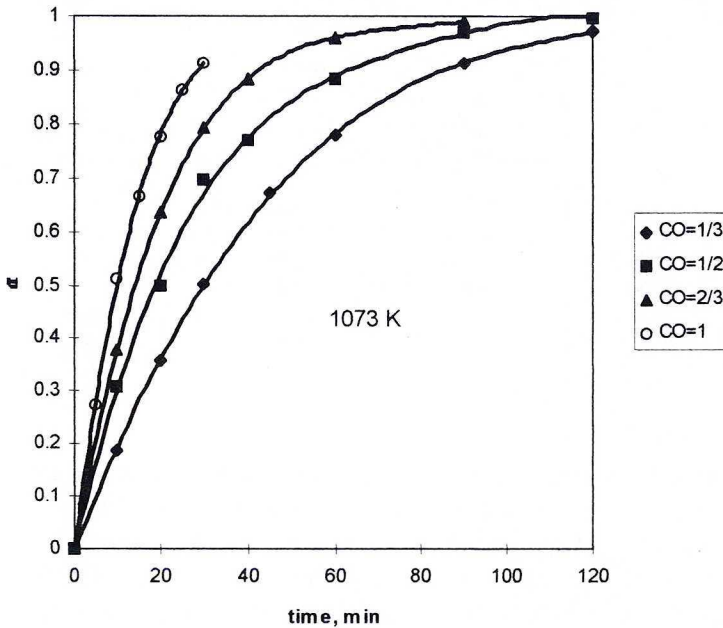


Fig. 2. Dependence of the degree of CdO reduction on the time of the process for various CO concentrations in the gaseous phase, at the temperature 1073 K

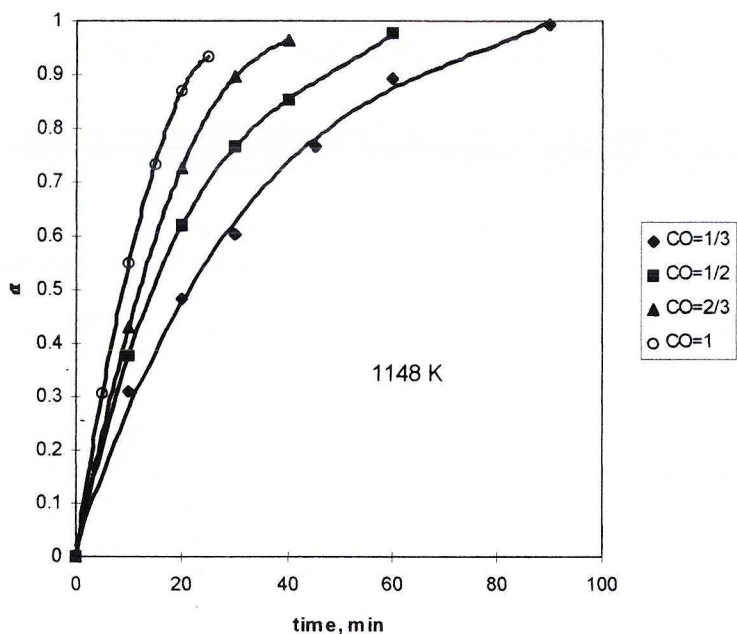


Fig. 3. Dependence of the degree of CdO reduction on the time of the process for various CO concentrations in the gaseous phase, at the temperature 1148 K

The total degree of CdO reduction, calculated on the basis of changes in the mass of the preparations, was additionally controlled on the basis of the results of chemical analysis for cadmium content, to which the remainder after the reduction was subjected. The calculated degree of reduction is listed in Table 3.

TABLE 3

The total degree of CdO reduction calculated on the basis of the results of chemical analysis and changes of mass

Flow of the gaseous phase phase [dm ³ /h]		Temperature of the process, [K]					
		1048		1073		1148	
		Degree of CdO reduction, [%]					
CO	CO ₂	accord. to chemical analysis	on the basis of mass change	accord. to chemical analysis	on the basis of mass change	accord. to chemical analysis	on the basis of mass change
15	30	93.80	94.09	96.90	97.26	99.17	99.48
22.5	22.5	98.90	97.50	99.13	99.81	—	—
30	15	99.09	99.83	99.43	98.89	—	—

The obtained results are evidence of good agreement, which is confirmed by the fact that when calculating the degree of CdO reduction on the basis of changes in the mass, corresponding up to 90% reduction of CdO, no great errors were made.

The selectivity of the course of the reduction reaction was controlled also through chemical analysis of dust, obtained after the reduction which contained partly oxidized cadmium and zinc vapours. The results of these analyses for the particular measurements variants are listed in Table 4. The obtained results indicate that the zinc content in zinc-cadmium dust is the greater the higher the temperature of the reduction process and CO concentration in the mixture of the reducing gases. The appearance of zinc in the gaseous reduction products results from the fact of partial ZnO reduction, which may occur only when CdO content is very small. If, however, the conditions of the condensation of cadmium and zinc vapours, presented in [3, 4] are taken into consideration, then in the condensation processes the composition of the gaseous phase will cause oxidization of Zn vapours. This will induce reoxidation of the vapours of zinc, which will form the so-called melting loss in the condenser. This should ensure obtaining of cadmium of higher than 99% purity, especially in the temperature range 1048—1073 K and CO concentration up to 50% in the gaseous phase.

TABLE 4

Results of chemical analysis of dust after the reduction processes

Flow of the gaseous phase, [dm ³ /h]		Temperature of the process, [K]					
		1048		1073		1148	
CO	CO ₂	Reduction degree of CdO, [%]	Zn content in the dust, [%]	Reduction degree of CdO, [%]	Zn content in the dust, [%]	Reduction degree of CdO, [%]	Zn content in the dust, [%]
15	30	98.72	0.85	99.01	1.44	99.17	1.46
22.5	22.5	98.90	1.64	99.13	1.65	99.22	1.64
30	15	99.09	1.93	99.43	1.48	99.46	2.07
45	0	99.25	1.80	99.46	1.84	99.82	4.47

For a mathematical description of the reduction process the following equation was used:

$$-\ln(1 - \alpha) = k \cdot t,$$

which, from among the equations cited in literature, describes best the process of CdO reduction. The calculated regression equations for the particular measurement conditions are listed in Table 5. The calculated values are indicative of a high correlation coefficient and small value of the initial ordinate for $t = 0$, which is theory should be equal to 0. The regression coefficient calculated in the equation, which is proportional to the reaction rate, was used to calculate the activation

TABLE 5

Parameters of equations describing the process of CdO reduction from oxides mixture (CdO+ZnO)

Temperature, [K]	CO concentration in the gaseous phase, [%]	$\ln(1-\alpha)$	Correlation coefficient, R^2
1048	33.3	$0.0233t - 0.0332$	0.9952
	50	$0.0314t + 0.0237$	0.9901
	66.7	$0.0504t - 0.0402$	0.9978
	100	$0.0737t - 0.0425$	0.9962
1073	33.3	$0.0255t - 0.0392$	0.9977
	50	$0.0362t + 0.0116$	0.9961
	66.7	$0.0527t - 0.0257$	0.9983
	100	$0.079t - 0.0531$	0.9965
1148	33.3	$0.0317t + 0.0171$	0.9969
	50	$0.0483t - 0.0032$	1.0000
	66.7	$0.065t - 0.0302$	0.9936
	100	$0.0883t - 0.039$	0.9934

energy. The value of the activation energy for the reduction reaction of CdO with (CdO+ZnO) mixture is the following:

- 840 ± 80 J/mol for CO content in the gaseous phase equal to 33.3%
- 1500 ± 200 J/mol for CO content in the gaseous phase from 50 to 100%.

Results, interesting from the point of view of zinc content in metallic cadmium and in dust, were obtained in the reduction tests of zinc-cadmium carbonate by means of carbon. The obtained results, presented in Table 6, show the possibility of obtaining cadmium of Cd-"0" grade, containing less than 0,1% of Zn.

Let us analyze the obtained results against the equilibrium concentrations of the Table 6 gaseous phase. At the reduction of the oxides mixture (CdO+ZnO) by

TABLE 6

Results of chemical analysis of products obtained at the reduction of zinc-cadmium carbonate by means of carbon

Temperature of the process, [K]	Zn content in cadmium, [%]	Content in dust, [%]		Content in the remainder, [%]	
		Zn	Cd	Zn	Cd
1200	3.13	0.40	95.62	28.83	9.81
	3.63	0.52	92.30	27.36	9.42
1173	0.28			29.94	1.58
1150	0.048	0.13	86.49	28.77	
1100	0.0035	0.076	92.91		

means of ($\text{CO} + \text{CO}_2$), the starting composition of the gaseous phase, even at low CO content, causes reduction of ZnO and CdO. When assuming simultaneous high reduction rate of CdO in comparison with ZnO, the composition of the gaseous phase in the reduction zone will make ZnO reduction impossible. Thus it should be assumed that partial reduction of ZnO could occur only when cadmium oxide had been reduced in a marked degree.

For the variant reduction of zinc-cadmium carbonate by means of carbon, with consideration given to Boudouard's reaction, the equilibrium concentrations of the gaseous phase result from the intersection of the straight line linking the characteristic points of the reduction reaction and Boudouard's reaction with the equilibrium curves for these reactions [6]. The composition of the gaseous phase in the reduction zone will oscillate, at the given temperature, between the equilibrium composition for the given reduction reaction and the equilibrium composition for Boudouard's reaction. Considering the rate of the course of these reactions, the composition of the gaseous phase at the temperature 1100 K will be closer to the equilibrium curve of CdO reduction, which will make the reduction of zinc oxide impossible. At higher temperatures of the process there should occur also partial ZnO reduction, which has been confirmed by experimental data.

3. Conclusions

The performed investigations of the selective course of the reaction of CdO reduction from the oxides mixture ($\text{CdO} + \text{ZnO}$) and from zinc-cadmium carbonate by means of the gaseous phase ($\text{CO} + \text{CO}_2$) and carbon allow to formulate the following conclusions:

1. The reaction of cadmium oxide reduction proceeds very fast above the temperature 1038 K, and the rate of this reaction is proportional to CO concentration in the mixture of gases ($\text{CO} + \text{CO}_2$).

2. In spite of high rate of the reaction of CdO reduction in comparison with the reaction of ZnO reduction, there takes place also partial reduction of ZnO, and the zinc content in the gaseous reaction products depends on the temperature of the process and on the starting composition of the gaseous phase ($\text{CO} + \text{CO}_2$). It is the greater the higher the CO concentration and the temperature of the process.

3. The determined value of the activation energy of the process was at the level 840 ± 80 J/mol for CO concentration in the gaseous phase equal to 33,3%, while at higher CO concentrations in the gaseous phase it amounted to 1500 ± 200 J/mol.

4. Obtaining pure cadmium of Cd-"0" grade or cadmium oxide of "C" grade is possible by reduction with carbon at the temperature 1100 K. Increasing of the temperature of the process causes the increase of zinc content in cadmium and of cadmium oxide.

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