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THE EFFECT OF THE GASEOUS PHASE COMPOSITION ON THE REDUCTION RATE OF CADMIUM OXIDE

WPŁYW SKŁADU FAZY GAZOWEJ NA SZYBKOŚĆ REDUKCJI TLENKU KADMU

The aim of the study was to determine the possibility of a selective reduction process of the oxide compounds of cadmium in the presence of zinc compounds. The performed investigation of reduction in the mixture of gases ($CO + CO_2$), of various composition and at different temperatures allowed to determine the conditions in which cadmium or cadmium oxide with a small content of zinc can be obtained.

Celem prezentowanej pracy było określenie możliwości selektywnego przeprowadzenia procesu redukcji tlenkowych związków kadmu w obecności związków cynku. Przeprowadzone badania redukcji w mieszaninie gazów ($CO + CO_2$), o różnym składzie oraz w różnych temperaturach, pozwoliły określić warunki, które umożliwią otrzymanie kadmu lub tlenku kadmu o małej zawartości cynku.

1. Introduction

Cadmium is the typical dispersed metal, which does not form isolated deposits, but accompanies the zinc ores. The mean ratio of zinc to cadmium in zinc concentrates varies within the limit 200—300. The metallurgy of cadmium is thus based mainly on the processing of various kinds of waste material and intermediate products of the zinc industry, in which cadmium compounds concentrate.

In obtaining cadmium two basic methods are used: the hydrometallurgical and the combined process. The hydrometallurgical method consists in obtaining a solution of cadmium sulfate, from which cadmium is obtained by way of electrolysis. In the combined method the so-called cadmium sponge is obtained through cementa-

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tion from a sulfate solution, which is next subjected to destillation in a reduction atmosphere.

In the hydrometallurgical process of zinc preparation the cadmium, present in the roasted ore and in the dust obtained in the course of roasting in the fluid state, passes to the solution during their leaching in a solution of sulfuric acid. Cadmium is precipitated from this solution by means of zinc in the form of the so-called cadmium sponge.

When the pyrometallurgical method of zinc preparation is applied, considerable amounts of cadmium pass to the dust during roasting on D-L machines. To recover cadmium from the dust, it is subjected to leaching, and next cadmium sponge or zinc-cadmium carbonate, containing 10—15% of Zn and about 40—45% of Cd, are precipitated from the solution. Preliminary information on the processing of this material directly into metallic cadmium can be found in the studies [1—2]. Cadmium sponge can be also melted into metallic cadmium under a layer of salt, however this process causes great loss of the material, and the obtained cadmium is contaminated with a marked content of zinc.

The aim of the present work is the determination of the effect of the composition of the gaseous phase ($CO + CO_2$) and the temperature on the reduction rate of cadmium oxide and on the zinc content in the products in the case of the reduction of the mixtures of cadmium and zinc oxides.

2. Determination of the conditions of a selective process of CdO reduction

Cadmium, as well as zinc, belong to those metals which, after reducton of their oxides, are obtained in the gaseous phase. As the system in which these reactions take place, at constant pressure and temperature, has 1 degree of freedom, the equilibrium compositions of the gaseous phase are illustrated by respective curves in the system Cd–CO–CO_2 and Zn–CO–CO_2. The composition of the gaseous phase in the equilibrium state thus depends on the starting composition. According to the opinion of Ptak and Sukiennik [3—4], the reactions, for which the sum of the stoichiometric coefficients occurring in the gaseous components of the reaction differs from zero, are characterized by the so-called characteristic point, and the compositions of the gaseous phase change as the reduction proceeds along the straight lines linking the starting state with the characteristic point. The composition of the gaseous phase in the state of equilibrium is defined by the point of intersection of the given straight line with the equilibrium curve of the respective reaction. Using the data [3—5], there have been calculated the equilibrium compositions of the gaseous phase for the reduction reactions of CdO and ZnO by means of CO, beginning with various starting compositions of the gaseous phase. In the calculations consideration has been given also to the course of the reduction reaction by means of carbon with simultaneous course of Boudouard's reaction. The equilibrium composition of the gaseous phase, as depending on the starting composition, has been calculated using the parametric equations [6]:

$$x_{CO} = [\lambda(x^{\circ}_{CO} + 1) - 1]$$

$$x_{CO_2} = [\lambda(x^{\circ}_{CO_2} - 1) + 1]$$

$$x_{Cd} = [\lambda(x^{\circ}_{Cd} - 1) + 1],$$

where:

x_{CO}, x_{CO_2}, x_{Cd} — equilibrium composition of the gaseous phase,
x°_{CO}, $x^{\circ}_{CO_2}$, x°_{Cd} — starting composition of the gaseous phase,
λ — parameter of the equation.

Making use of the dependence:

$$K = \frac{x_{CO_2} \cdot x_{Cd}}{x_{CO}} = \frac{[\lambda(x^{\circ}_{CO_2} - 1) + 1][\lambda(x^{\circ}_{Cd} - 1) + 1]}{[\lambda(x^{\circ}_{CO} + 1) - 1]},$$

the parameter λ was determined for the given composition of the starting phase, and next the equilibrium composition of the gaseous phase was calculated. The calculation results are listed in Table 1.

These results show that the composition of the gaseous phase in the state of equilibrium depends on the composition of the starting phase. With increasing CO concentration in the starting gaseous phase, there will increase the CO_2 and the cadmium concentration in the system. For a given starting composition of the gaseous phase the temperature has a minimal effect on the change of the equilibrium composition of the gaseous phase.

For the reduction reaction of zinc oxide $ZnO + CO = Zn_1 + CO_2$ at temperatures below 1180 K, the equilibrium compositions of the gaseous phase are as follows:

$$T = 1048\ K \qquad x_{CO} = 0.9966 \qquad x_{CO_2} = 0.0034$$

$$T = 1073\ K \qquad x_{CO} = 0.9958 \qquad x_{CO_2} = 0.0042$$

These values show the possibility of the reduction of zinc oxide by means of CO. In the case of co-reduction with cadmium oxide, the composition of the gaseous phase with be shifted towards higher contents of CO_2 which will oxidize the probably reduced zinc passing to the gaseous phase as the pressure of zinc vapours above liquid zinc at the temperature 1048 K equals 170,88 mm Hg. If we assume that after ZnO reduction zinc appears in the gaseous phase, then the equilibrium composition of the gaseous phase at the temperature 1100 K will be:

$$x_{CO} = 0.868 \qquad x_{CO_2} = 0.066 \qquad x_{Zn} = 0.066$$

TABLE 1

Equilibrium composition of the gaseous phase for the reduction $CdO + CO = Cd_g + CO_2$ depending on the starting composition of the gaseous phase (in molar fraction)

Temp. [K]	Starting phase composition		Equilibrium composition of the gaseous phase		
	x°_{CO}	$x^{\circ}_{CO_2}$	x_{CO}	x_{CO_2}	x_{Cd}
1048	1/3	2/3	0.000270	0.74993	0.249800
	1/2	1/2	0.000350	0.66655	0.333100
	2/3	1/3	0.000375	0.59985	0.399775
	1	0	0.000400	0.49980	0.499800
1073	1/3	2/3	0.0002000	0.749950	0.249850
	1/2	1/2	0.0002750	0.666575	0.333150
	2/3	1/3	0.0002917	0.599883	0.399825
	1	0	0.0003000	0.499850	0.499850

The performed investigations show that it is highly probable to select such temperature of the process and the composition of the gaseous phase that they will secure the selective course of the reduction process of cadmium oxide from a material containing zinc oxide.

3. Experimental results and their discussion

Investigations of the reduction were carried out on pure cadmium oxide and on material containing 49.95% of Cd and 16.8% of Zn, obtained after roasting zinc-cadmium carbonate at the temperature 1073 K. The experiments were performed in an electric pipe furnace through which a gaseous phase with a definite content of CO and CO_2 was passed. The aim of the experiments conducted on pure cadmium oxide was the determination of the effect of temperature and CO concentration in the gaseous phase on the reduction rate of CdO. On the other hand, the experiments conducted on material containing zinc and cadmium oxides were expected to provide the answer to the question how the CO_2 concentration in the gaseous phase and temperature of the process affect the zinc content in the gaseous products of the reduction. The degree of cadmium oxide reduction, calculated on the basis of recorder losses of mass during the process, is shown in Fig. 1. Similar dependences were obtaine for other temperatures.

For a mathematical description of the occurring process of reduction there has been adapted the equation in the form [7—8]:

$$\sqrt[3]{(1-\alpha)^2} = A - k \cdot t,$$

where:

α — degree of reduction,
t — time of the process [min],
k — constant proportional of the reaction rate [min^{-1}],
A — starting co-ordinate, which for $t = 0$ should be equal to 1.

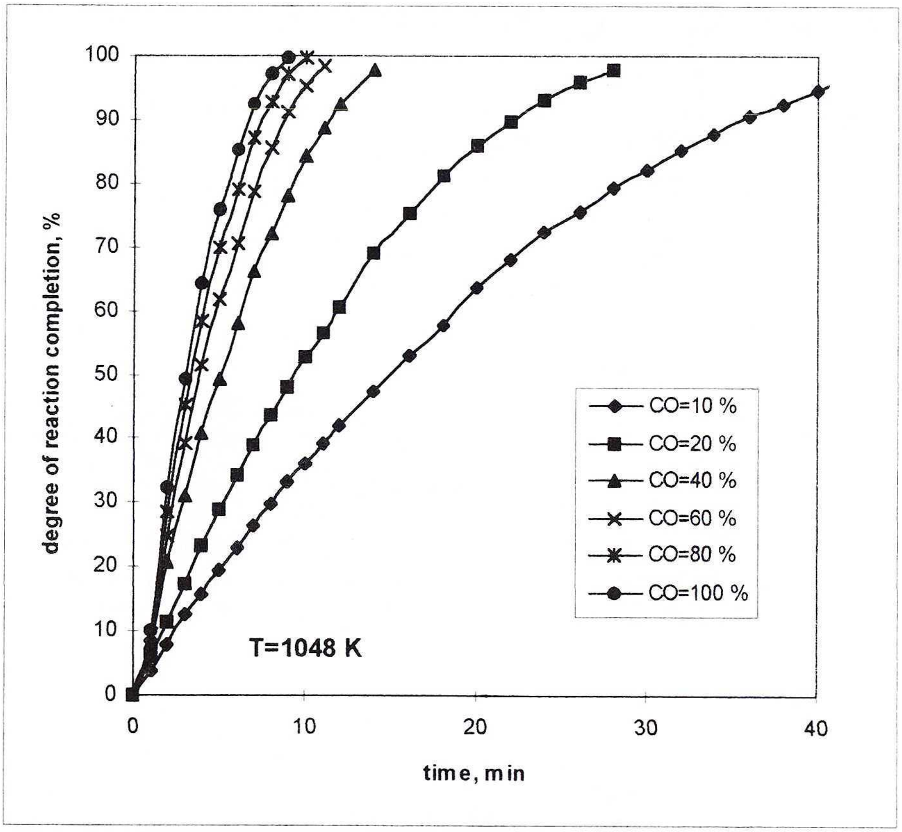

Fig. 1. Degree of CdO reduction depending on the duration of the process at the temperature 1048 K for various CO contents in the gaseous phase

The parameters of the kinetic reactions, calculated on the basis of experimental data, are listed in Table 2, while Fig. 2 illustrated the course of the calculated equations at the temperature 1073 K against the background of experimental points. In the final phase of the process the reduction rate becomes distinctly diminished in relation to the course resulting from the calculated equation. This follows from the gradual transformation of the cylindrical shape of the starting sample into a spherical shape, which means reduced surface of reaction for the same mass of a sample obtained as a result of incomplete reaction.

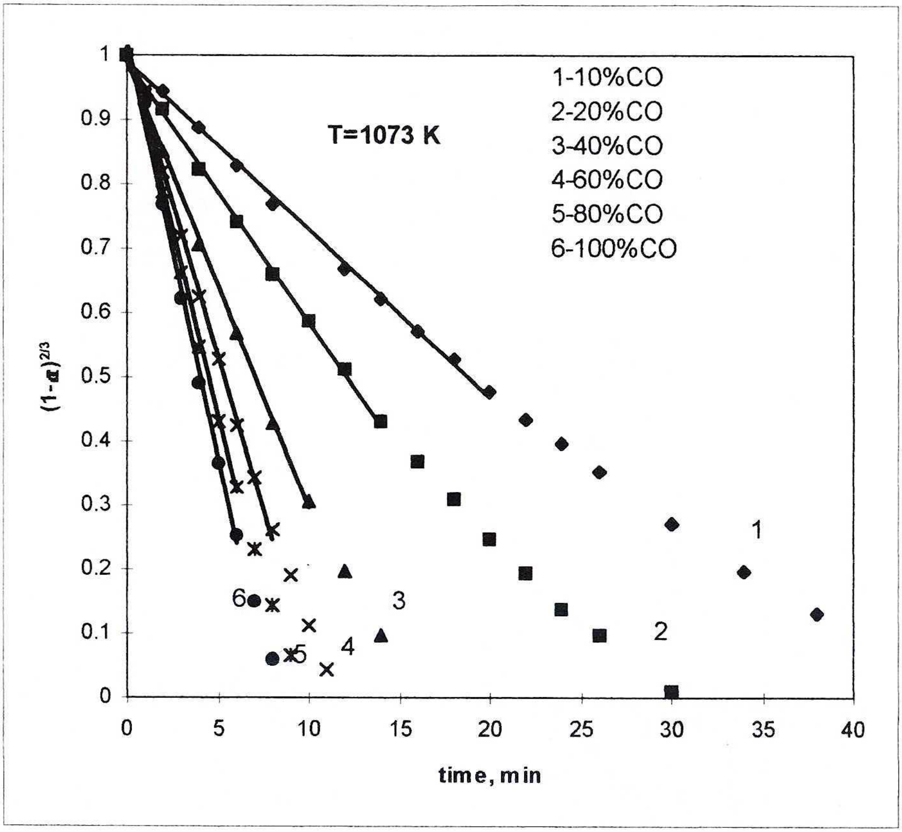

Fig. 2. The course of the calculated kinetic equations against the background of experimental points for the temperature 1073 K, at various CO content in the gaseous phase

TABLE 2

Calculated values of the kinetic equation

Temp. [K]	CO in the gaseous phase, [%]	A	*k*
1048	10	0.9877	0.0236
	20	0.9930	0.0380
	40	0.9994	0.0717
	60	1.0109	0.0941
	80	1.0192	0.1127
	100	1.0210	0.1255
1073	10	0.9902	0.0261
	20	0.9914	0.0404
	40	0.9911	0.0696
	60	1.0112	0.0955
	80	1.0211	0.1166
	100	1.0212	0.1300

When analyzing the changes in the value of the regression coefficient we find that the temperature of the reduction process affect in a minimal degree the rate of the process, whereas the CO content in the gaseous phase has a significant effect on it. If we assume that the rate of the reduction process at constant temperature is proportional to the distance from the equilibrium state by:

$$\Delta x_{CO} = x^{\circ}_{CO} - x_{CO}$$

where:

x°_{CO} — concentration of carbon oxide in the starting gaseous phase [%],
x_{CO} — concentration of carbon oxide in the gaseous phase in the state of equilibrium [%],

and assuming, on the basis of the performed calculations, that $x_{CO} = 0$ then the reaction rate is proportional to x°_{CO}.
Having to our disposal the values of k for various x°_{CO} contents at constant temperature, the mutual relation between these values was determined. It has been defined by the relation:

$$k = a \cdot (x^{\circ}_{CO})^{n}$$

where:

a, n — equation constant.
The equation parameters calculated on the basis of linear regression analysis gave the following values:

$T = 1048$ K	$a = 0.0042$	$n = 0.7494$
$T = 1073$ K	$a = 0.0049$	$n = 0.7191$

In both cases the correlation coefficient was higher than 0.997.

In the further part of the study there have been carried out the investigations of CdO reduction from an oxide material containing zinc and cadmium oxides. The aim of these investigations was to test whether under conditions of intense reduction of cadmium oxide there takes place a simultaneous reduction of zinc oxide. As the conditions in which the reduction process was carried out did not allow the condensation of cadmium vapours, the conclusions concerning the selectivity of the reduction process will be drawn on the basis on analysis of the obtained dust for the content of zinc and the analysis of the remainder after reduction for the content of cadmium. The investigations were carried out at the temperatures 1048, 1073 and 1148 K, at various CO content in the starting gaseous phase.

Changes of the mass in the samples, registered during reduction have shown that the relative loss of the sample mass was the greater, the higher the CO content in the flowing gaseous phase. The total relative loss of the mass of the samples resulting only from CdO reduction should be equal to 52,5%. The experimental results indicated that especially at higher temperatures of the process and with higher CO contents in the gaseous phase this value was exceeded. This fact may be an indication that in these conditions the zinc oxide was also reduced. This observation has been confirmed by the results of chemical analysis listed in Table 3.

TABLE 3

Zinc and cadmium content in the reduction products

Temperature [K]	CO in the gaseous phase [%]	Relative loss of mass [%]	Cd content in the remainder [%]	Zn content in the dust [%]
1048	33	49.40	1.16	0.85
	50	51.19	1.03	1.64
	67	52.41	0.88	1.93
	100	54.16	0.75	1.80
1073	33	52.76	0.96	1.44
	50	52.40	0.84	1.65
	67	51.92	0.54	1.48
	100	54.97	0.55	1.84
1148	33	52.23	0.80	1.46
	50	53.21	0.76	1.64
	67	56.04	0.33	2.07
	100	62.08	0.19	4.47

The obtained results may be interpreted as indicating that it is not possible to obtain metallic cadmium of high purity from oxide material containing zinc and cadmium by way of reduction. When the composition of the gaseous phase and the conditions of the condensation of zinc and cadmium vapours are taken into consideration, it may be stated that in the gaseous phase when it passes from the reactor to the condenser there exist conditions favouring the reoxidation of zinc vapours which in the condenser may form the so-called melting loss, which enables to obtain metallic cadmium of high purity.

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