

THE INITIAL SURFACE STRUCTURE OF Co_3O_4 AS A FACTOR OF INFLUENCE ON KINETIC FEATURES OF THE DISSOLUTION OF THE SOLID PHASE

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Abstract

Due to the depletion of natural reserves of cobalt-containing ores, it is urgent to optimize the processes of cobalt replenishment, based on the leaching of its compounds, processing of industrial waste, regeneration of cobalt compounds from catalysts. The kinetic characteristics of the dissolution of metal oxides are influenced by the initial state of their surface structure, which requires the accumulation of experimental material and individual targeted studies. The paper presents the results of an experimental study of the surface structure of industrial Co_3O_4 cobalt oxide samples. The studies were carried out by electron microscopy and X-ray phase analysis and revealed the size and shape of the Co_3O_4 particles and the nature of their surface distribution. The correspondence of experimental and theoretical data has been established, Co_3O_4 cobalt oxide has been identified as an α -form of the cubic crystal system. The data obtained are of interest in the study of the effect of the surface characteristics of the solid phase of Co_3O_4 cobalt oxide on the dissolution kinetics under the chemical and electrochemical influence

Keywords

Cobalt oxide, surface structure, electron microscopy, X-ray diffraction analysis, dissolution kinetics

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Introduction. Given the reduction in natural reserves of cobalt ores in Russia, the task of finding new technologies and optimal conditions for the separation of cobalt compounds from depleted ores is very important [1–5]. Despite the accumulation of experimental material on the dissolution of cobalt oxides, research in this area does not lose its relevance.

The choice of cobalt compounds is due to the importance of cobalt as a component of promising structural materials, a catalyst in organic chemistry, an alloying component in heat-resistant steels.

Various technologies for the production of materials determine the differences in their surface properties (composition, structure, morphology). In turn, the parameters of the processes of the interaction of the solid phase with electrolyte solutions depend, among other factors, on the state of the surface of the studied samples [6–8]. In this regard, the study of the surface properties of solid phases chemically or electrochemically interacting with electrolyte solutions is an important factor in the characterization of processes occurring on the surface of the sample and in the volume of the liquid phase of the solution.

The purpose of the work is to study the surface characteristics of Co_3O_4 cobalt oxide to identify the subsequent effect of the structure of the samples on the kinetic parameters of their chemical and electrochemical dissolution in acid electrolytes.

Materials and methods. For research, we used samples of industrial Co_3O_4 cobalt oxides (Technical Requirements 6-09-4680–78) of qualification “chemically pure”. The methodology for sample preparation was as follows. Powdered oxides were fractionated and fractions of 80–100 μm in size were selected for studies. Samples were washed with bidistilled water for 30 min, then stabilized at 250 °C during the 24-hour day, continuously blowing with oxygen, which was obtained by electrolysis.

Surface studies of the initial samples of Co_3O_4 oxides for their identification and determination of the crystal structure were performed by electron microscopy using an electron microscope *REM LEO 1420 (Carl Zeiss)* and X-ray diffraction analysis (DRON-3 diffractometer, $\text{CuK}\alpha$ radiation).

Research results and discussion. On the obtained micrographs of particles of Co_3O_4 cobalt oxide, when passing from a smaller to a larger increase, individual particles of the samples and details of their structure become distinguishable.

By their shape, the particles of Co_3O_4 cobalt oxide are distorted-shaped microspheres that are inhomogeneous in magnitude, mostly approaching spherical (Fig. 1). An increase in the multiplicity from 5.00X to 25.00X and 101X made it possible to detect the presence of a well-developed surface with sufficiently wide and deep pores. Particles are combined into agglomerates, the size of which varies.

Based on the statistical processing of micrographs, a histogram of the distribution of Co_3O_4 cobalt oxide particles was constructed (Fig. 2 a), which

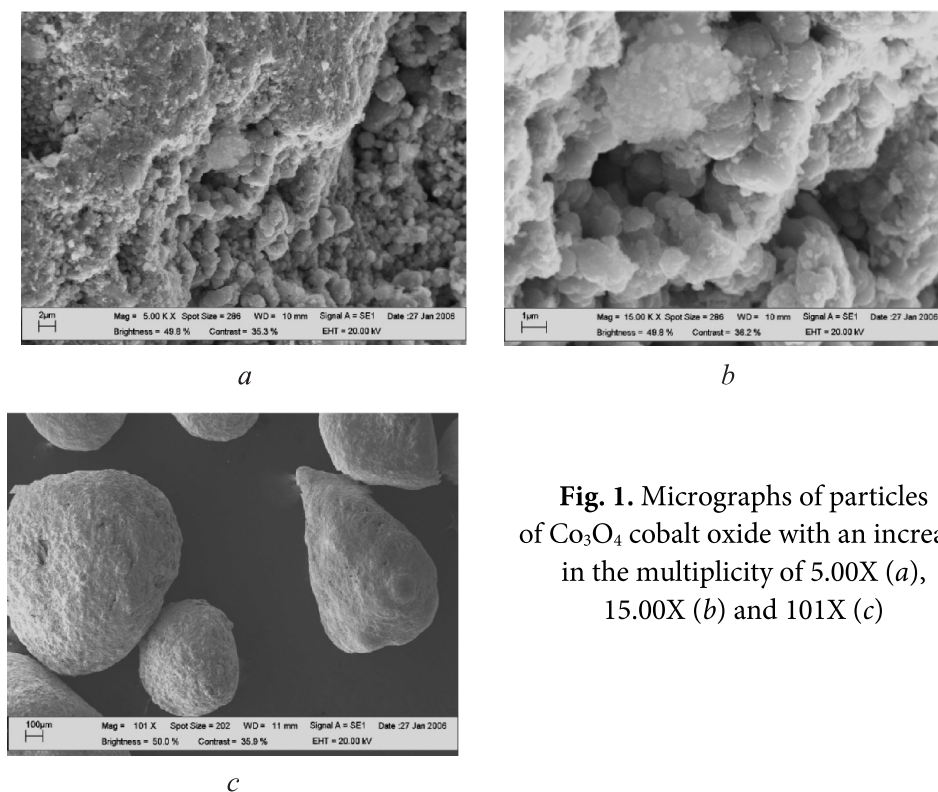


Fig. 1. Micrographs of particles of Co_3O_4 cobalt oxide with an increase in the multiplicity of 5.00X (a), 15.00X (b) and 101X (c)

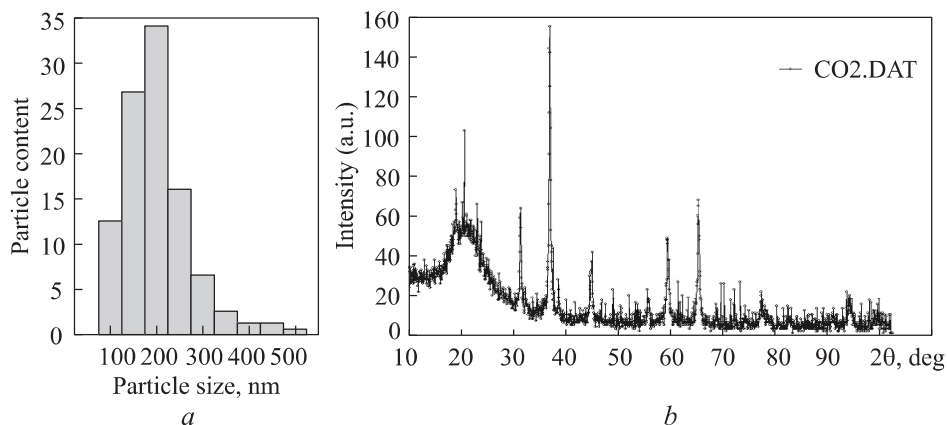


Fig. 2. The histogram of the distribution of particles of cobalt oxide Co_3O_4 by size (a) and X-ray diffraction pattern for Co_3O_4 cobalt oxide particles (b)

indicates a significant proportion of the coarse fraction. The maximum distribution falls on the average size parameter of about 200 nm.

The X-ray diffraction pattern for Co_3O_4 cobalt oxide particles (Fig. 2 b) was obtained in the range of angles $2\theta = 10\text{--}102^\circ$ with a scan step of $\Delta 2\theta = 0.05^\circ$ and exposure time at $t = 4$ s (monochromatic radiation $\text{CuK}\alpha$, $\lambda = 1.5405 \text{ \AA}$).

The experimental data of the X-ray phase analysis and the results of the identification of the Co₃O₄ cobalt oxide compound using theoretical data are given in Tables 1–3.

Table 1

Experimental data of X-ray diffraction analysis of Co₃O₄ cobalt oxide particles

2 θ , deg	19.03	31.34	36.92	38.55	44.85	55.73	59.41	65.28	77.46	94.10	99.35
d , nm	4.6594	2.8521	2.4327	2.3333	2.0190	1.6480	1.5543	1.4281	1.2311	1.0524	1.0100
I , %	12	24	100	6	20	8	32	41	7	9	3

Table 2

Identification results of Co₃O₄ cobalt oxide compound (I , α -form), theoretical data

hkl	d_{exp} , Å	I_{rel} , %	2 θ_{exp} , deg	2 θ_{calc} , deg	$\Delta 2\theta$, deg
1 1 1	4.6646	12	19.01	18.99	0.02
2 2 0	2.8526	34	31.33	31.26	0.07
3 1 1	2.4333	100	36.91	36.84	0.07
2 2 2	2.3305	9	38.60	38.54	0.06
4 0 0	2.0185	19	44.87	44.80	0.07
4 2 2	1.6502	8	55.65	55.64	0.01
5 1 1	1.5551	33	59.38	59.34	0.04
4 4 0	1.4290	38	65.23	65.22	0.01
5 3 3	1.2322	7	77.38	77.32	0.06
6 4 2	1.0804	3	90.95	90.94	0.01
7 3 1	1.0528	7	94.05	94.06	-0.01
8 0 0	1.0118	3	99.15	99.30	-0.15

Cubic crystal system, sp.gr. $Fm\bar{3}m$, $a = 8.085(2)$ Å.

Table 3

Identification results of Co₃O₄ cobalt oxide compound (β -form)

hkl	d_{exp} , Å	I_{rel} , %	2 θ_{exp} , deg	2 θ_{calc} , deg	$\Delta 2\theta$, deg
1 1 1	4.6594	12	19.03	19.01	0.02
2 2 0	2.8521	24	31.34	31.29	0.05
3 1 1	2.4327	100	36.92	36.87	0.05
2 2 2	2.3333	6	38.55	38.57	-0.02
4 0 0	2.0190	20	44.85	44.83	0.02
4 2 2	1.6480	8	55.73	55.69	0.04
5 1 1	1.5543	32	59.41	59.39	0.02

End of the Table 3

hkl	$d_{exp}, \text{Å}$	$I_{rel}, \%$	$2\theta_{exp}, \text{deg}$	$2\theta_{calc}, \text{deg}$	$\Delta 2\theta, \text{deg}$
4 4 0	1.4281	41	65.28	65.27	0.01
5 3 3	1.2311	7	77.46	77.39	0.07
7 3 1	1.0524	9	94.10	94.16	-0.06
8 0 0	1.0100	3	99.35	99.40	-0.05

Cubic crystal system, sp.gr. $Fm\bar{3}m$, $a = 8.079(2) \text{ Å}$.

The calculated and experimental values of angle 2θ are in good correspondence with each other, and the existing deviations are less than the measurement error. A comparison of experimental and theoretical data showed that Co_3O_4 cobalt oxide is represented by the α -form of cubic crystal system.

Conclusion. The authors studied the surface structure of nanoparticles of industrial Co_3O_4 cobalt oxide (Technical Requirements 6-09-4680-78). Using the method of electron microscopy, it was found that Co_3O_4 cobalt oxides used as a solid phase are represented by particles of a rounded shape with a well-developed surface in the form of sufficiently wide and deep pores.

The diagram of the weight distribution of the nanoparticles of Co_3O_4 cobalt oxide particles indicates a significant proportion of the coarse fraction. The average particle size of approximately 200 nm accounts for the maximum weight distribution.

X-ray phase analysis showed that particles of Co_3O_4 cobalt oxide are formed by the α -form of cubic crystal system. A comparison of experimental and theoretical data made it possible to confirm the identification of the Co_3O_4 cobalt oxide compound.

The data obtained are of interest as a factor in the influence of the surface state at the dissolution kinetics of Co_3O_4 cobalt oxide and the use of this oxide as an absorbent [9–15].

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