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PHASE TRANSFORMATIONS OF ALUMINIUM HYDROXIDE IN THE CALCINATION PROCESS

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ABSTRACT

In this paper phase transformations were considered that occur in the process of calcination of aluminium hydroxide, and for qualitative phase analysis low-temperature X-ray analysis was used. Two samples were used, one of chemical purity obtained under laboratory conditions and the other obtained under industrial conditions in the alumina production plant at Kidričevo, Yugoslavia.

It was determined that for both samples in the process of calcination of aluminium hydroxide identical transformations appear, and the sequence of transformations present may be shown in the following way:

$$\alpha\text{-Al(OH)}_3 \rightarrow \text{AlOOH} \rightarrow \gamma \rightarrow \eta \rightarrow \theta \rightarrow \kappa \rightarrow \alpha\text{-Al}_2\text{O}_3$$

INTRODUCTION

Research of phase transformations of aluminium hydroxide in the calcination process has a large practical significance because aluminium oxides, obtained by calcination of different samples of aluminium hydroxide, differ in their physical and chemical characteristics.

A large number of articles on the subject of identification of phase transformations appearing in the aluminium hydroxide calcination process has been published so far. However, there is no strictly defined opinion about what exactly happens in this process. A predominant line of thought is that during thermal decomposition in the atmosphere of air α-Al(OH)$_3$ decomposes to AlOOH which transforms into a dehydrated aluminium oxide which suffers a series of phase transformations with increase of temperature and that the final product in all cases is α-Al$_2$O$_3$. Results achieved by research in this area may be summarized in the following way:

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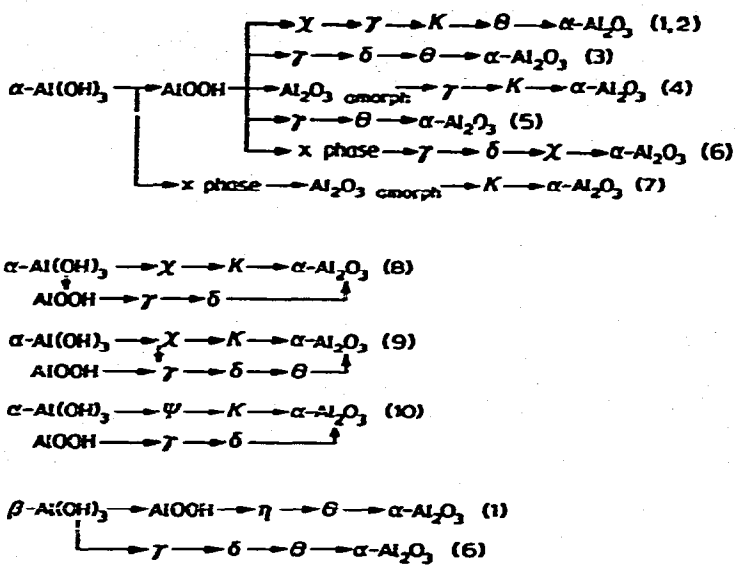

For the identification of phase transformations which are present in the process of calcination of aluminium hydroxide, the authors whose results have been presented above, use in the majority of cases low-temperature and high-temperature X-ray diffraction analysis or infrared spectroscopy.

EXPERIMENTAL

For research of phase transformations present in the process of calcination of aluminium hydroxide in the temperature range from 298 to 1673 K, low-temperature X-ray diffraction analysis was used and research was done on a sample of aluminium hydroxide obtained under laboratory conditions and on a sample of aluminium hydroxide obtained under industrial condition in the alumina production plant at Kidričevo.

X-ray diffraction analysis was done on the equipment produced by the Siemens. Recording was done with Cu anti-cathode and filtrated emission by Ni-filter at a voltage of 40 kV and a current of 18 mA. For registration of reflected emission a scintillation detector was used.

RESULTS AND DISCUSSION

The content of impurities, specific mass and specific surface of samples being studied are presented in Table I. It is obvious that there exists a difference in the specific surface of samples studied as well as in the content of impurities. In both cases the content of Na_2O is the highest and the content of all impurities in the sample taken from the alumina production plant at Kidričevo does not exceed 0.5%.

In all cases samples of aluminium hydroxide to be studied were heated in an atmosphere of air at the rate of 10°C min^{-1} to the required temperature at which they

TABLE 1

SOME OF THE CHARACTERISTICS OF SAMPLES STUDIED

Sample	*Specific weight* ($kg\ m^{-3}$)	*Specific surface* ($m^2\ kg^{-1}$)	*Impurities (%)*					
			SiO_2	Fe_2O_3	V_2O_5	TiO_2	CaO	Na_2O
Chemically pure	2530	315	—	—	—	—	—	0.15
Kidričevo	2530	84.5	0.009	0.027	0.001	0.002	0.018	0.16

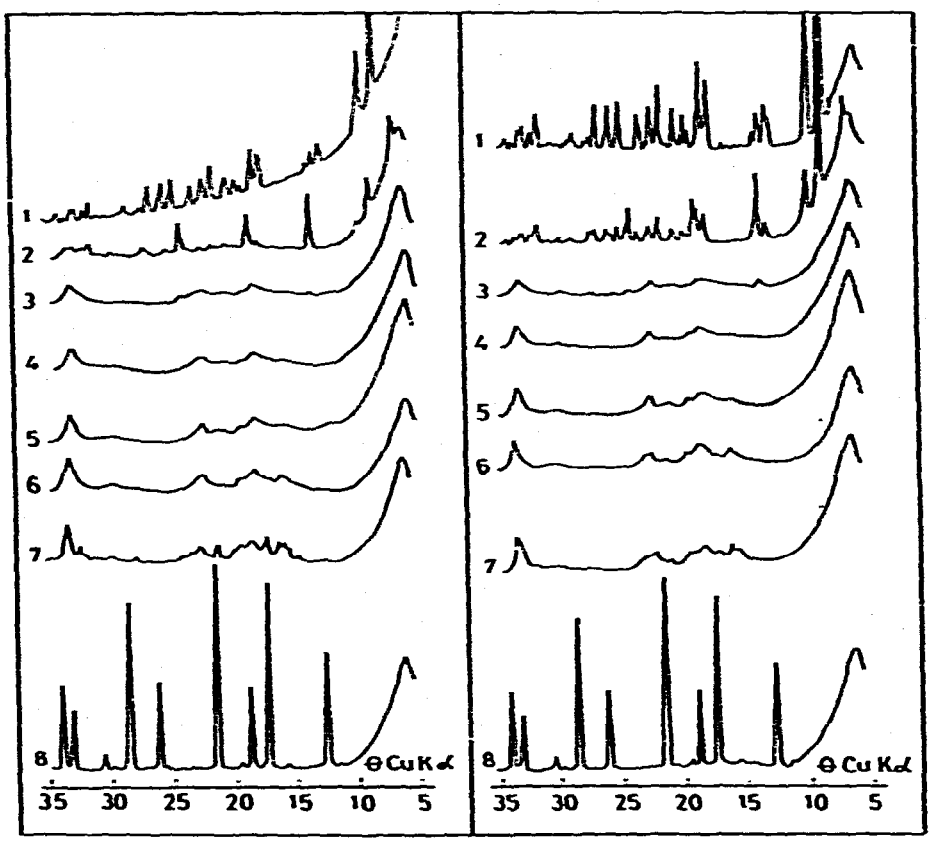

Fig. 1. Roentgenograms of aluminium hydroxide thermally treated at different temperatures. (a) Chemically pure sample. (b) The sample from the alumina plant at Kidričevo. 1 = 298 K; 2 = 573 K; 3 = 773 K; 4 = 873 K; 5 = 973 K; 6 = 1173 K; 7 = 1273 K; 8 = 1573 K.

were held for about 60 min and then quickly cooled to room temperature. Samples prepared in such a way were analyzed by X-ray diffraction analysis in order to determine phases appearing in the process of heating to the required temperature. Considering the fact that there is a low probability of having a reversed reaction during the process of cooling the sample, it may be considered that phases determined in such a way are identical to those appearing at the reaction temperature.

TABLE 2

RESULTS OF QUALITATIVE PHASE ANALYSIS

No. reflections	*Roentgenogram No. 1*			*Roentgenogram No. 2*			*Roentgenogram No. 3*			*Roentgenogram No. 4*		
	d(Å) compared to ASTM for α-Al(OH)₃	*$d_{calc.}$ (Å)*		*d(Å) compared to ASTM for AlOOH*	*$d_{calc.}$ (Å)*		*d(Å) compared to ASTM for γ-Al₂O₃*	*$d_{calc.}$ (Å)*		*d(Å) compared to ASTM for γ-Al₂O₃*	*$d_{calc.}$ (Å)*	
		Chem. pure	*Kidričevo*		*Chem. pure*	*Kidričevo*		*Chem. pure*	*Kidričevo*		*Chem. pure*	*Kidričevo*
1	4.85	4.87	4.84	6.11	6.13	6.09	4.56	—	—	4.56	—	—
2	4.37	4.39	4.36	3.164	3.164	3.155	2.80	2.43	2.40	2.80	2.86	2.82
3	3.32	3.32	3.34	2.346	2.342	2.337	2.39	2.39	2.39	2.39	2.39	2.39
4	3.306	—	3.298	1.980	1.984	1.984	2.28	2.27	2.27	2.28	2.27	2.27
5	3.183	3.186	3.169	1.860	—	—	1.977	1.980	1.97	1.977	1.975	1.976
6	3.112	3.104	3.091	1.850	1.849	1.851	1.520	1.520	1.51	1.520	—	—
7	2.454	2.456	2.448	1.770	1.776	1.764	1.395	1.389	1.388	1.395	1.392	1.394
8	2.420	2.423	2.413	1.662	1.569	1.658	1.140	—	—	1.140	—	—
9	2.388	2.385	2.378	1.527	1.525	1.524	1.027	—	—	1.027	—	—
10	2.285	2.289	2.283	1.453	1.449	1.451	0.989	—	—	0.989	—	—
11	2.244	2.245	2.237	1.434	1.430	1.432	0.884	—	—	0.884	—	—
12	2.168	2.165	2.157	1.412	1.408	1.408	0.806	—	—	0.806	—	—
13	2.085	2.085	2.043	1.396	1.393	1.398						
14	2.043	2.049	2.014	1.383	1.380	1.380						
15	1.993	1.994	1.987	1.363	—	—						
16	1.960	1.959	1.955	1.312	—	—						
17	1.9..1	1.916	1.912									
18	1.799	1.801	1.799									
19	1.750	1.748	1.746									
20	1.689	1.688	1.679									
21	1.654	1.656	1.650									
22	1.638	1.637	1.632									
23	1.593	1.588	1.586									
24	1.584	—	—									
25	1.573	1.572	1.569									
26	1.555	1.552	1.547									
27	1.551	—	1.528									
28	1.486	1.481	1.480									
29	1.477	—	—									
30	1.457	1.455	1.452									
31	1.441	1.437	1.435									
32	1.409	1.408	1.405									
33	1.398	1.399	1.396									
34	1.380	—	—									

No. of reflections	Roentgenogram No. 5			Roentgenogram No. 6			Roentgenogram No. 7			Roentgenogram No. 8		
	d(Å) compared to ASTM for η-Al_2O_3	$d_{calc.}$ (Å)		d(Å) compared to ASTM for 0-Al_2O_3	$d_{calc.}$ (Å)		d(Å) compared to ASTM for κ-Al_2O_3	$d_{calc.}$ (Å)		d(Å) compared to ASTM for α-Al_2O_3	$d_{calc.}$ (Å)	
		Chem. pure	Kidričevo		Chem. pure	Kidričevo		Chem. pure	Kidričevo		Chem. pure	Kidričevo
1	4.60	—	—	5.20	—	—	6.20	—	—	3.479	3.480	3.491
2	2.80	—	—	4.50	4.56	4.52	4.50	4.51	—	3.552	3.556	2.556
3	2.40	2.39	2.40	3.53	—	—	4.20	—	—	2.379	2.380	2.378
4	2.27	2.28	2.28	2.85	2.84	2.83	3.04	3.04	3.03	2.165	2.163	2.161
5	1.97	1.98	1.98	2.72	2.72	2.72	2.79	2.80	2.80	2.085	2.088	2.088
6	1.52	1.57	1.52	2.56	2.57	2.56	2.70	—	2.72	1.964	1.963	1.959
7	1.40	1.39	1.39	2.43	2.44	2.44	2.57	2.57	2.57	1.740	1.737	1.737
8	1.21	—	—	2.31	—	—	2.41	2.42	2.43	1.601	1.600	1.600
9	1.14	—	—	2.24	2.26	2.25	2.32	2.33	2.32	1.546	1.543	1.542
10	1.03	—	—	2.11	2.12	2.12	2.26	2.26	2.27	1.514	—	—
11				2.01	1.99	1.99	2.16	2.16	2.16	1.510	1.508	1.508
12				1.91	1.95	1.94	2.11	2.11	2.11	1.404	1.404	1.400
13				1.80	1.79	1.79	2.06	2.06	2.08	1.374	1.371	1.371
14				1.73	—	—	1.99	1.99	1.98	1.337		
15				1.61	—	—	1.95	1.95	1.95	1.276		
16				1.54	1.53	1.53	1.87	1.87	—	1.239	—	—
17				1.49	1.51	1.50	1.82	1.82	—	1.2343	—	—
18				1.45	—	—	1.74	1.74	—	1.1898	—	—
19				1.43	—	—	1.64	1.64	1.63	1.1600	—	—
20				1.40	—	—	1.54	1.54	1.53			
21				1.39	1.389	1.388	1.49	1.48	1.48			
22				1.34	—	—	1.45	1.44	1.44			
23				1.29	—	—	1.43	1.43	1.43			
24				1.26	—	—	1.39	1.387	1.386			
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Characterisation of phases by X-ray diffraction analysis was done on samples which were previously treated thermally at the following temperatures: 573, 773, 873, 973, 1173, 1273 and 1573 K as well as on samples treated at 298 K.

Roentgenograms obtained for the sample of chemical purity (a) and for the sample obtained under industrial conditions in the alumina plant at Kidričevo (b) are shown in Fig. 1.

The qualitative phase analysis, based on roentgenograms obtained was done such that intersurface distances "*d*" were calculated in ångströms and the values obtained compared with values of "*d*" for the required reflections from ASTM cards.

From roentgenograms shown it may be seen that reflections with $Al(OH)_3$ sample of chemical purity are less prominent as compared to the sample taken under industrial conditions, which is effected also with other phases up to roentgenograms for samples that were thermally treated at 1573 K when reflections were very prominent in both cases. This may be the consequence of the smaller diameter of particles of the starting sample of aluminium hydroxide of chemical purity.

On roentgenograms for samples that were thermally treated at temperatures of 773 to 1273 K less prominent reflections may be observed, which is the consequence of decreasing the size of particles during the calcination process of aluminium hydroxide. This phenomenon has led some of the authors[4, 7] to the wrong conclusion that amorphous aluminium oxide is formed in the process of calcination. At temperatures higher than 1273 K processes of recrystallization are effected so that prominent reflections are obtained on roentgenograms for these products.

Based on roentgenograms shown in Fig. 1, Table 2 shows calculated values of intersurface distance "*d*" with corresponding values from ASTM cards.

Results obtained (see Table 2) show that for samples studied, which were thermally treated at the particular temperature, in all cases for both samples identical reflections appear, which shows that in the process of calcination of aluminium hydroxide obtained under industrial conditions the same transformations appear.

The starting sample in both cases represents the α-modification $Al(OH)_3$ while reflections for β-$Al(OH)_3$ were not registered. At 573 K appearance of bemite is registered, at 773 K γ-Al_2O_3 with a certain quantity of residual AlOOH at 873 K only γ-Al_2O_3 appears, at 973 K η-Al_2O_3, at 1173 K θ-Al_2O_3, at 1273 K apart from θ and κ-Al_2O_3 appears and finally at 1573 K only α-Al_2O_3 appears which represents the final product in the process of calcination of aluminium hydroxide.

It may be seen that for the sample obtained under industrial conditions, in all cases, in corresponding phases for corresponding reflections lower intersurface distances are observed as compared to the sample of chemical purity. This difference decreases at higher temperatures so that with α-Al_2O_3 almost identical intersurface distances are obtained.

Accordingly, it may be concluded that in the process of calcination of aluminium hydroxide the following transformations appear:

$$\alpha\text{-}Al(OH)_3 \rightarrow AlOOH \rightarrow \gamma \rightarrow \eta \rightarrow \theta \rightarrow \kappa \rightarrow \alpha\text{-}Al_2O_3$$

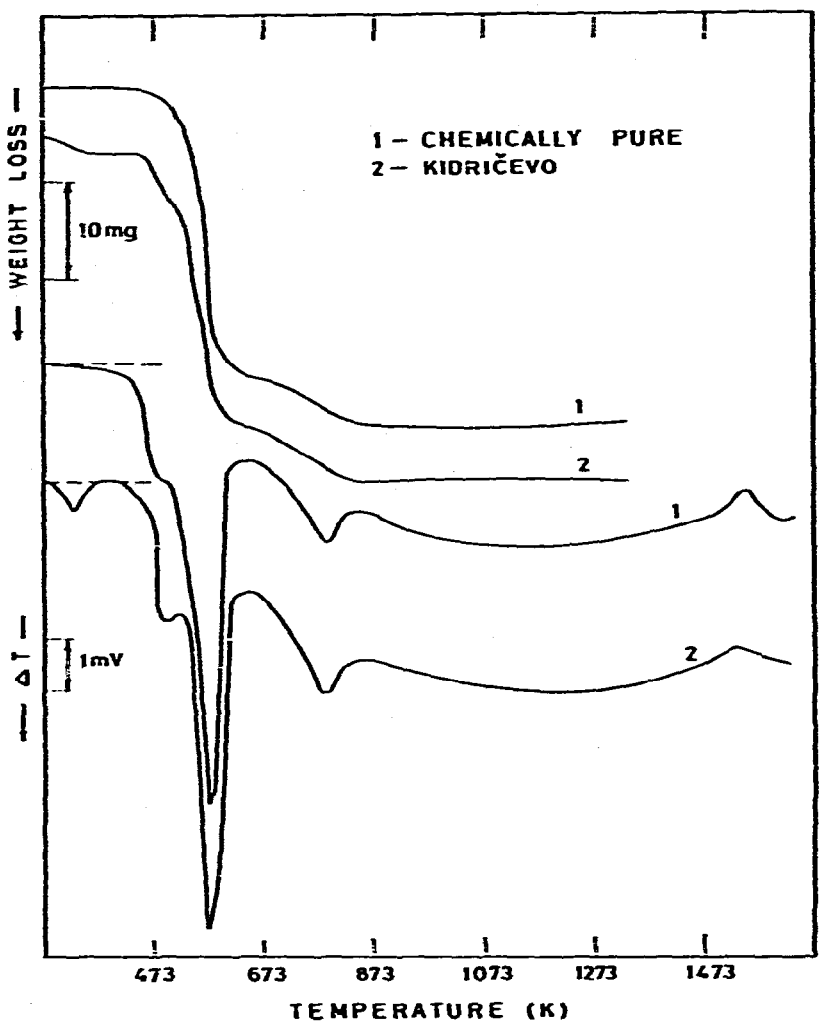

Fig. 2. TG and DTA curves for samples of aluminium hydroxide studied in an atmosphere of air at a heating rate of 10°C min^{-1}.

and that for both samples studied the sequence of phase transformations is identical.

Some of these transformations may be registred by thermogravimetric analysis (TG) and differential thermal analysis (DTA) as is shown in Fig. 2.

The dehydratation process of α-$Al(OH)_3$ to AlOOH and of AlOOH to γ-Al_2O_3 on TG curves is shown in units of weight loss and DTA curves. It is clearly defined by endothermal peaks, endothermality of the former being far higher than the latter. On DTA curves the process of crystallization of α-Al_2O_3 is also registered by an exothermal peak at 1573 K which has a variable intensity depending on the particle size of the starting $Al(OH)_3$. There is no corresponding explanation for the appearance of the peak. Other transformations in the process of calcination of aluminium hydroxide are followed by weak heat effects and this is the reason why they can not be registered by DTA equipment. In certain cases an exothermal peak may appear at about 1173 K,

which is not reproductive, so that for its occasional appearance there is no corresponding explanation.

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