Thermochimica Acta, 233 (1994) 97–105
Elsevier Science B.V., Amsterdam
SSDI 0040-6031(93)01301-I

Thermal decomposition of low-grade high-silicon boehmite bauxite

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(Received 22 February 1993; accepted 5 April 1993)

Abstract

The results of investigations during the thermal treatment of low-grade high-silicon and high-iron boehmite bauxite from Western Serbia are reported.

The results indicate that the basic minerals constituting the investigated bauxite are mutually isomorphous, so that the eventual enrichment of these bauxites by separation of the basic minerals (boehmite, kaolinite and haematite) is only possible by exploiting differences in their chemical properties. Physical methods of separation are not helpful because the initial isomorphism of the minerals is retained during thermal decomposition.

INTRODUCTION

The thermal decomposition of bauxite has been thoroughly investigated with respect to the kinetics and mechanism of its decomposition [1–4]; various thermoanalytical methods have been applied to identify the single phase that developes during the thermal decomposition of various types of bauxites [5–7].

Because of the presence of increased amounts of associated minerals (kaolinite, hematite, geothite, rutile, etc.), it is difficult to interpret the processes that occur during heating of low-grade bauxite due to its complex structure.

The investigations reported here present a comparative study of the processes that take place during the thermal treatment of a low-grade high-silicon, and high-iron boehmite bauxite.

EXPERIMENTAL

Low-grade boehmite bauxite, from Užice in Western Serbia, was used for the experiments. The chemical composition and mineralogical structure of the bauxite are given in Table 1. The levels of rare metals present, as

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TABLE 1

The chemical composotion and mineralogical structure of the tested bauxite

Chemical composition		Mineralogical structure	
Component	Content %	Component	Content %
Al_2O_3	40.83	Boehmite	30.85
SiO_2	17.41	Kaolinite	30.21
Fe_2O_3	26.65	Hematite	26.65
TiO_2	2.30		
CaO	0.22		
MgO	0.54		
MnO	0.06		
Ignition loss	11.20	Ignition loss	11.20
Total	99.21	Total	98.91

determined by mass spectrometry, are under 0.01%, which is in accord with numerous other bauxites.

Thermal analyses were performed on a derivatograph (MOM, Budapest), X-ray diffractometry on a Siemens apparatus with a Cu anti-cathode and a Ni filter, electron microanalysis on a Cambridge electron microscope, IR spectroscopy on a Perkin-Elmer 180 spectrometer from 4000 to 200 cm^{-1}, and electronic paramagnetic resonance studies on a Joel-3BX spectrometer.

DISCUSSION

Figure 1 shows the simultaneous DTA–TG–DTG analysis for the investigated low-grade bauxite. An endothermic peak appears at 560°C, corresponding to the overlapping dehydration processes of boehmite and kaolinite. The exothermic peak at 910°C corresponds to the formation of mullite, as a consequence of the reaction between the γ-Al_2O_3 and SiO_2 formed by the decomposition of kaolinite.

X-ray analysis of the initial bauxite, thermally treated at 600 and 950°C (Fig. 2), indicates that the basic starting components are boehmite, kaolinite and haematite. Following annealing at 600°C, the X-ray diffraction peaks of boehmite disappear because it transforms into γ-Al_2O_3 whose particles are too fine to yield a diffraction pattern [7]. No kaolinite is registered, because its thermal decomposition yields γ-Al_2O_3 and amorphous SiO_2. When bauxite is annealed at 950°C, in addition to some hematite, mullite phase is registered, but it is not clearly defined because much of it is in a glassy form.

Scanning electron microscopy of the initial bauxite particles, as well as of bauxite particles calcinated at 600 and 950°C, indicates the presence of

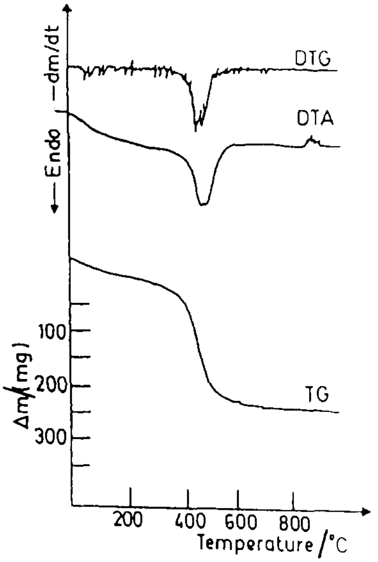

Fig. 1. DTA–TG–DTG analysis of bauxite; heating rate, 10 K min^{-1}.

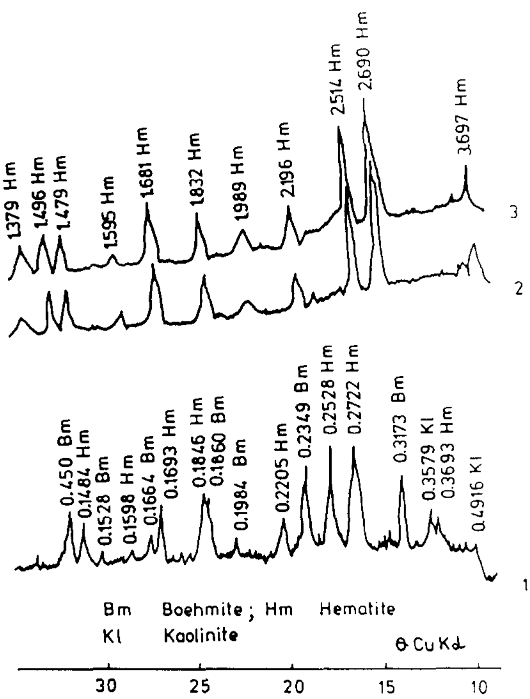

Fig. 2. X-ray diffractogram for the starting bauxite (1), and for bauxite calcinated at 600°C (2) and 950°C (3).

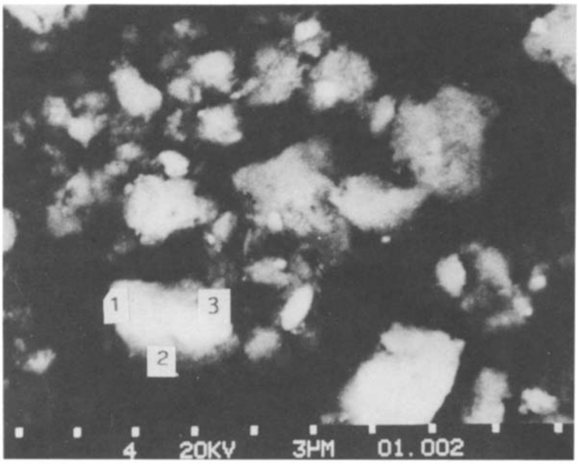

Fig. 3. SEM micrograph of bauxite, original magnification, 4000 ×.

heavy (Fe) and light (Al, Si and Ti) elements in the studied samples; the electron micrographs are illustrated in Figs. 3–5.

The results obtained indicate approximately the same composition all over the surface of the starting sample, up to particle sizes of 3 μm. On heating the bauxites at 600°C, when kaolinite and boehmite dehydrate, it can be seen that the particles become spherical and that the light elements, predominantly Si, concentrate on the particle surfaces; this is even more apparent in bauxite calcinated at 950°C. In this case, mullite phase in a glassy state is present and this causes formation of the spherical particles and Si diffuses to the particle surfaces.

Semi-quantitative chemical analyses of the surface at designated points in Figs. 3–5 are shown in Figs. 6–8, respectively. The results obtained

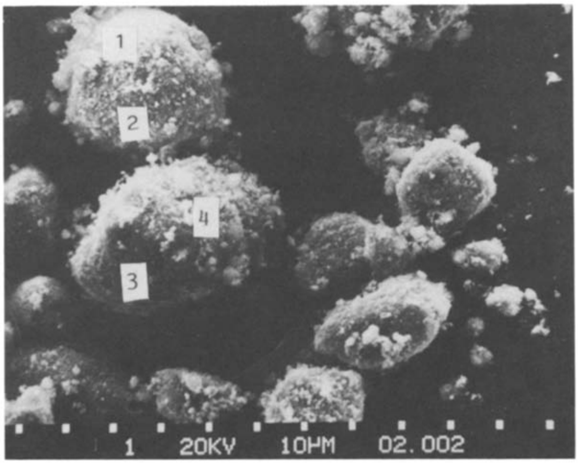

Fig. 4. SEM micrograph of bauxite after thermal treatment at 600°C; original magnification, 750 ×.

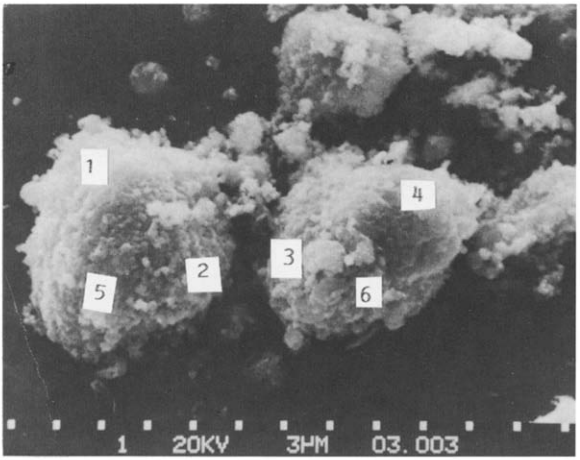

Fig. 5. SEM micrograph of bauxite after thermal treatment at 950°C; original magnification, 3000 ×.

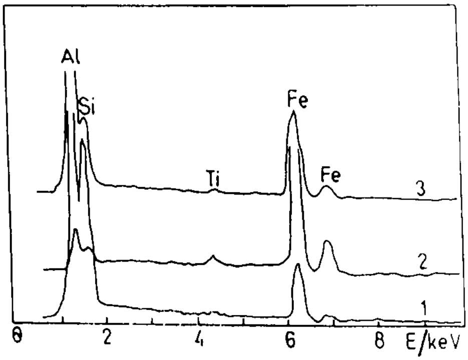

Fig. 6. X-ray microanalysis of the bauxite at points designated in Fig. 4.

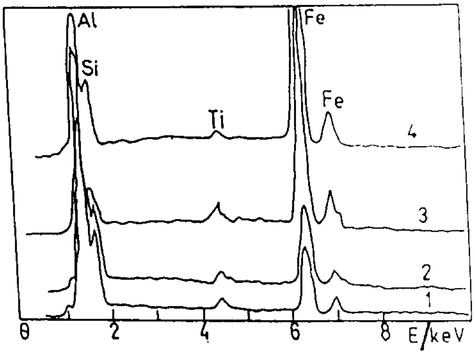

Fig. 7. X-ray microanalysis of the bauxite at points designated in Fig. 5.

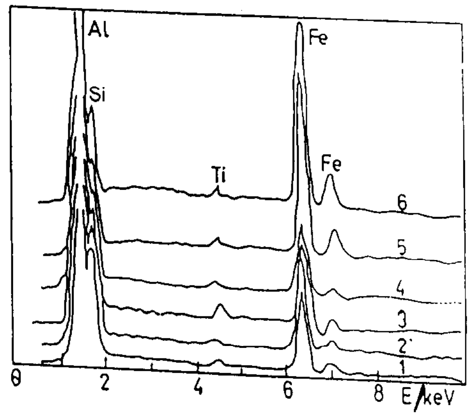

Fig. 8. X-ray microanalysis of the bauxite at points designated in Fig. 6.

indicate that the Al, Si and Fe contents, which determine the quality of the bauxite and the technological possibilities of its processing, are approximately uniform in particles of around 10 μm. This indicates that bauxite may be enriched by processes based on differences in the physical characteristics of the constituent minerals following grinding of the bauxite down to particle sizes of 10 μm; this is not realistic in technological and economical terms. However, by studying the influence of the crystal lattice, it may be possible to determine if the basic minerals can be separated when greater particle sizes are present.

The infrared spectra of the samples were recorded on a Perkin-Elmer 180 in the 4000–200 cm^{-1} range using the Nujol mull technique. The results are summarized in Table 2.

Table 2 reveals that sample 1, the initial bauxite, contains boehmite AlOOH, gibbsite $Al(OH)_3$ and kaolinite $Al_4(Si_4O_{10})(OH)_8$. The presence of the bands observed at 915 cm^{-1}, 940 cm^{-1} (δ(OH) of gibbsite), 3100 cm^{-1}, 3295 cm^{-1} (ν(OH) boehmite), 1070 cm^{-1}, 1150 cm^{-1} (δ(OH)), and at 3695 cm^{-1}–3625 cm^{-1} (δ(OH)) of kaolinite confirms this. The band at around 1000 cm^{-1} is overlapped by those originating in ν_{as} (Si–O–Si) vibrations which result from the silicates present in the sample. The same overlap has been detected within the 400–300 cm^{-1} range, where the deformation vibrations of SiO_4^- tetrahedra usually appear [8–12]. A band due to M–O (where M denotes an iron or aluminium ion) stretching vibration has been observed in the spectra of all the samples, but an additional band assignable to the ($M–OH_2–M$) vibration [10] has been detected in the spectrum of sample 1 at 650 cm^{-1}.

The spectra of samples 2 (calcinated at 600°C) and 3 (calcinated at 950°C) show neither this feature, nor those of the ν(OH) vibration at 3100 and 3290 cm^{-1} characteristic of boehmite. Nor were bands at 915 cm^{-1} and 3625 cm^{-1} due to gibbsite vibrations observed in these spectra. This is quite

TABLE 2

Results of the IR spectroscopy of bauxite samples: sample 1, without calcination; sample 2, calcinated at 600°C; sample 3, calcinated at 950°C

Wavenumber/cm^{-1}			Vibrations
Sample 1	Sample 2	Sample 3	
325			SiO_4^{4-}
345	340	350	SiO_4^{4-}
365			SiO_4^{4-}
400	400	405	SiO_4^{4-}
485	470	485	M–O, M is Fe, Al
540	550	565	M–O, M is Fe, Al
650			M_1–OH–M_2, $M_{1,2}$ is Fe, Al, ν_{as}
725	720	725	Si–O–Al
750	735	740	Si–O–Al
915			Al ··· O–H gibbsite, δ(OH)
940			Al ··· O–H
1010			Si–O–Si, ν_{as}
1035			Si–O–Si, ν_{as}
1070	1065	1095	Si–O–Si boehmite, δ(OH), ν_{as}
1150	1140	1150	Si–O–Si boehmite, δ(OH), ν_{as}
1650	1650	1650	H–OH, moisture
3100			Al ··· O–H, boehmite, ν(OH)
3295			Al ··· O–H boehmite, ν(OH)
	3400	3440	O–H moisture
3625			Al ··· O–H, gibbsite
3650			Al ··· O–H, kaolinite
3695			Al ··· O–H, kaolinite

understandable because these samples were prepared from sample 1 by heating. The bands at 1650 cm^{-1} and 3400 cm^{-1} are due to the δ(OH) and ν(OH) vibrations of adsorbed water.

The results of our studies clearly indicate that the heat treatment causes the destruction of the boehmite (orthorhombic), and gibbsite (monoclinic and triclinic) layer structures. Nevertheless, the occurrence of the bands (480–570 cm^{-1}) characteristic of metal–oxygen vibrations [13–14] suggests that the admixtures of aluminium and iron ions are permanently bound by the remaining atoms, chiefly oxygen, in either distorted tetrahedra or distorted octahedra in all the samples.

Electron paramagnetic resonance spectra were recorded for all three samples on a Jeol-3BX spectrometer at 77 and 300 K.

The results were investigated using the following spin-Hamiltonian [15]

$$\hat{H}_s = g_1\beta H\hat{S}_z + g_2\beta H\hat{S}_x + g_3\beta H\hat{S}_y + D[\hat{S}_z^2 - \tfrac{1}{3}S(S+1)] \\ + E(\hat{S}_x^2 - \hat{S}_y^2) + a_1\hat{S}_z^4 + a_2(\hat{S}_x^4 + \hat{S}_y^4)$$

where $a_1 \gg a_2$.

TABLE 3

The values of spin-Hamiltonian parameters: sample 1, without calcination; sample 2, calcinated at 600°C; sample 3, calcinated at 950°C

Sample	Values of parameters					
	g_1	g_2	g_3	E/cm^{-1}	D/cm^{-1}	a_1/cm^{-1}
	Temperature, 300 K					
1	4.276	1.999		0.655	0.432	−0.042
2	4.237	1.970		0.659	0.435	−0.042
3	4.256	1.969		0.662	0.437	−0.042
	Temperature, 77 K					
1	4.338	2.034	1.767	0.637	0.419	−0.040
2	4.296	1.861		0.707	0.469	−0.046
3	4.276	2.029		0.645	0.425	−0.041

The results are summarized in Table 3. Analysis of the data indicate that $E > D$, because all the samples exhibit a signal with $g > 4$. The results also indicate that the Fe^{3+} ions are located in a crystal field of tetragonal symmetry. It seems quite possible that Fe^{3+} occupies Al^{3+} sites in the crystal lattice in all three samples studied. These studies confirm the results of an earlier IR spectral investigation which also indicated the close proximity of the Fe^{3+} and Al^{3+} ions. Therefore, the problems associated with the removal of iron from the bauxite ore are apparent.

CONCLUSIONS

The investigations into changes in the physico-chemical characteristics during thermal treatment of low-grade bauxites from the region of Western Serbia (Yugoslavia) have yielded the following conclusions.

(a) The structure of the studied bauxite is such that the arrangement and concentration of the basic elements Al, Fe and Si, are approximately uniformly arranged in particles up to 10 μm in size, which indicates that separation of the basic minerals, boehmite, hematite and kaolinite, according to differences in physical features, is perhaps only possible when the particles are smaller than 10 μm, which is neither economically nor technologically possible.

(b) The asymetric vibration at 650 cm^{-1} indicates a bond within the starting bauxite (Fe–OH–Al) that can be destroyed by heating, but the vibrations corresponding to the Me–O bonds (where Me is Al, Fe) remain, even in calcinated bauxites. EPR spectra confirm the results of the IR investigations and indicate a tetragonal symmetry of the Fe^{3+} ions in the crystal lattice, with a possibility of Fe^{3+} changing places with Al^{3+} in the crystal lattice of the starting bauxite as well as in the calcinated bauxites.

(c) The extraction of the contaminating Fe_2O_3 and SiO_2 present in the crystal lattice of this bauxite is only possible by chemical reaction with suitable reagents, which would allow for the selective dissolution of unwanted components and, thus, for an enrichment of the bauxite which could then be processed by Bayer's process for the production of alumina. A detailed study of possible reagents for the enrichment of these low-grade bauxites and an interpretation of the results obtained are the subject of a separate study.

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