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OPERATING TECHNIQUE OF MILLS IN THE PROCESS OF MICRONIZATION MILLING OF ALUMINA

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Abstract

This paper summarized under the title: "Operating technique of mills in the process
of micronization milling of alumina" is occupied with micronization of alumina and its influences on change of alumina crystal structure; the research is based on existing scientific and technical-technological findings and experiences in the field of development and application of processes of the materials.
In short, this research task involves:

- investigation of initial material effects on kinetics and mechanism of the particle formation together with the phase transformations occurring in the process,

- characterization of materials,

- consideration of close relations between theoretical principles of operation of high-energy mills, such as vibrational and planetary mills during the micronized of alumina which obeyed the certain laws, with their dependance on selected experimental conditions,

- detailed investigation of the possibility to obtain high-grade αAl_2O_3 alumina in the form of micronic, nonagglomerated particles by the method of dry micronized combined with heat treatment, and starting from the γAl_2O_3 alumina modification after the Bayern process.

The elements that are necessary for determination of operation of mills, particularly vibrational and planetary ones, were determined by

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detailed investigation of the alumina micronized; also, conditions required to define the both technological and production parameters of micronization are fulfilled, too.

Based on investigated parameters and theoretical consideration of the alumina micronized, together with its influences on change of the alumina crystal structure by usage of mills with advanced construction and contemporary instrumental techniques used in determination and observation of the most important physical, chemical and thermic characteristics, kinetic model which is the basis for a quick and efficient determination of above parameters in order to optimize and automize micronization processes was developed.

Key words: *micronization, vibrational and planetary mills coarsness, specific surface area, specific energy consumption, structure.*

1. Introduction

Phisical, chemical and mineralogical properties of γAl_2O_3, alumina modification obtained after the Bayern process, could be improved by processing of micronization. Characteristics of treating alumina satisfy all requirements for its usage in chemical industry, metallurgy, agrochemistry, ceramic industry, constructional materials as well as in refractory materials. Increase of the alumina reactivity to the value of 32-40% αAl_2O_3 was realized by micronization of γAl_2O_3 alumina in high-energy vibrational and planetary mills with micronization time of 240 min. According to the previous considiration, it was concluded that the combination of both processes, micronization and thermal treatment of alumina is the most successful way to achieve following aims: increasing of alumina reactivity, complete phase transformation of γAl_2O_3 to αAl_2O_3, and obtaining of alumina with appropriate properties.

2. Materials and methods

Tall investigations of dry micronization were realized in the following high-energy mills: vibrational mill with balls type, "Veskefama-GMBH-SM06", and planetary ball mill type, "Retsch-PM4". For physical characteri-

zation, multichannel coarseness analyzer "Coulter Electronics-Multisizer" was used, the X-ray analyses were performed by automatic diffractometer "Philips PW1710", IR spectra were obtained by FT IR spectrometer "Bomem-Hartman and Michelson MB-100", the shape factor, average grain diameter and specific surface were determined by electron microscope "Joel JSM-T20". Materials used in this investigation were γ-alumina obtained by the Bayer process in Aluminium Combine-Podgorica and the reference alumina "Alcoa" (2) .

3. Applied methodology of experimental results analysis

Analitical presentation of several parameters: the grain size composition (d'-average particles diemeter-coarseness, d_{95}-aperture of sieve that pass through 95% of mechanical activated material, n-directional coefficient, St and Sr-theoretical and actual values of specific area) as well as analitical procedure of processing parameters determination (Q-mills capacity, e-specific energy consumption, etc.) are described in the scope of this part of the paper (1, 6) .

3.1. Analitical presentation of grain size composition

It was noticed long ago, that shapes of cumulative characteristics of coarseness due to pulverization of raw materials satisfy functional dependance between average diameter d', and cumulative oversize R and undersize D values.

A few different analytical equations were proposed by several authors. Rosin-Rammler equation is the most applicable formula in practice. It is defined by following exponential formula:

$$R = 100e^{-\left(\frac{d}{d'}\right)^{n}} \qquad (1)$$

where: R - is the cumulative oversize value, %
e - is the natural logarithm (with the base of e=2,718),
d - is the sieve aperture, mm,
d' - is an average grain diameter-coarsness, mm.

In the case of following equality, d=d', the value of R is 36,79%, so the parameter d' characterizes sample coarsnessand sieve aperture with R=36,79%, as well.

Below equation is obtained by double logarithm of "Rosin-Rammler" formula (1):

$$\log\log\frac{100}{R} = n\log d - n\log d^{\copyright} + \log\log e \qquad (2)$$

In the coordinate system (logd; loglog100/R), this equation has appearance of straight line with certain direction coefficient, n. Binary logarithms network is used for determination of parameters d' and n; logarithm of sieve aperture is placed to the ordinate while the binary logarithms of 100/R is placed to the apscise. Coordinate axis of the n-parameter is added to the above network of coordinates by Sperling (1, 6). Therefore, diagram of grain size composition that is drawn on that manner, is called RRS-(Rosin-Rammler-Sperling) diagram.

Also parameters d' and n could be obtained by following analytical procedure: two points are chosen on the curve of grain size composition; they should be at the most distance from each other; curves fitting through the points are equations with two unknown quantities, d' and n:

$$\log\log\frac{100}{R_1} = n\log d_1 - n\log d' + \log\log e \qquad (3)$$

or

$$\log\log\frac{100}{R_2} = n\log d_2 - n\log d' + \log\log e \qquad (4)$$

eq. (5) is followed from eq. (4):

$$\log d' = \frac{n\log d_2 + \log\log e - \log\log\left(\frac{100}{R_2}\right)}{n} \qquad (5)$$

Below eq. is obtained by substitution of value of logd' from the eq.(5) to the eq.(3) as well as by solvation of this eq. according to n:

$$n = \frac{\log\log\frac{100}{R_1} - \log\log\frac{100}{R_2}}{\log d_1 - \log d_2} \tag{6}$$

Parameter d_{95}, i.e. sieve aperture that pass through 95% of micronized material is determined by calculation of exponential equation (1).

$$\ln R = \ln 100 + \left[-\left(\frac{d}{d'}\right)\right]\ln e \tag{7}$$

or

$$\left(\frac{d}{d'}\right)^n = \ln 100 - \ln R \tag{8}$$

or

$$n\left(\ln d - \ln d'\right) = \ln\ln 100 - \ln\ln R \tag{9}$$

or

$$n\ln d - n\ln d' = \ln\ln 100 - \ln\ln R \tag{10}$$

or

$$\ln d = \frac{\ln\ln 100 - \ln\ln R + n\ln d'}{n} \tag{11}$$

and finally:

$$d_{95} = e^{\left(\frac{n\ln d' + \ln\ln 100 - \ln\ln R}{n}\right)} \tag{12}$$

where: d_{95} - is the aperture of sieve that pass through 95% of micronized material,

d' - is the average grain diameter-coarseness, mm,

e - is the natural logarithm (with the base od e=2,718), and

R - is the cumulative oversize, %.

The values of n, d' and d_{95} are determined by appliances of equations (5), (6) and (12), by usage of known values of sieve aperture (d_1 and d_2), and by employment of cumulative oversizes (R_1 and R_2); values of d_1, d_2, R_1 and R_2 could be found in the Table 1-6 of micronization aluminas grain-size composition.

3.2. Specific area

Theoretical specific area S_t, is very important characteristic of material that is exposed to micronization; S_t could be obtained on the basis of average diameter that is found during the RRS-procedure, by below eq.:

$$S_t = \frac{6.39}{\rho \cdot d'} e^{\frac{1.795}{n^2}} \qquad (13)$$

where: S_t - is the theoretical specific area, m^2/kg,
d' and n - parameters of Rosin-Rammler eq., d' in m,
e - is the natural logarithm (with the base od e=2,718), and
ρ - is the sample destiny, kg/m^3.

Actual specific area S_r could be calculated by formula:

$$S_r = f \cdot S_t \qquad (14)$$

3.3. Analytical procedure of processing parameters determination

Values obtained during the experiments with certain time of micronization as well as familiar equations (15-17) are used with the aim of analytical and calculated determination of processing parameters such as the capacity of high-energy vibrational and planetary mills (Q) and the specific consumption of energy (e).

3.3.1. Capacity of high-energy mills

During the materials activation, capacity and specific energy consumption are depended on the amount of activated material and the time of activation, too.

However, capacity of high-energy mills is directly proportional to the amount of activated material, but it is an inverse proportion of the time of activation, so:

$$Q = \frac{G}{t} \tag{15}$$

where: Q - is the capacity of mills, kg/h,
G - is the mass of dry micronized sample, kg, and
t - is the time of milling, h.

3.3.2. Specific consumption of energy

With the aim of characterization of mechanical activation, specific cosumption of energy is determined by below formula:

$$e = \frac{E}{G} = \frac{N \cdot t}{G} \tag{16}$$

Following equation is obtained by substitution of t-value from the equation (15) to the equation (16), so:

$$e = \frac{N}{Q} \tag{17}$$

3. Results and discussion

During the experiments of alumina micronization, variable parameters of mills operation (time, number of revolutions and vibrations, specific energy) as well as characteristic parameters of obtained products (the specific surface, the shape factor, the average diameter, the calcination temperature, X-ray and IR analysis) were followed.

In the Table1, results obtained by investigation of grain size composition of the initial and reference aluminas samples are presented. In the Table 2 the same data are given for the final product obtained by micronized (3, 4).

Table 1. Grain size composition of initial and reference aluminas samples
M-Mass portion (%); R-Cumulative oversize (%); D-Cumulative undersize (%)

Alumina	Initial sample			Reference sample		
Size class in μm	M % mass portion	R % oversize	D % undersize	M % mass portion	R % oversize	D % undersize
-63+20	2.26	2.26	100.00	0.70	0.70	100.00
-20+15	12.23	14.49	97.74	0.80	1.50	99.30
-15+10	20.50	34.99	85.51	1.70	3.20	98.50
-10+5	16.00	50.99	65.01	3.80	7.00	96.80
-5+3	15.66	66.65	49.01	2.70	9.70	93.00
-3+2	12.69	79.34	33.35	1.10	10.80	90.30
-2+1	10.36	89.70	20.66	7.70	18.50	89.20
-1+0	10.30	100.00	10.30	81.50	100.00	81.50
Total	100.00	-	-	100.00	-	-

Table 2. Grain size composition of the final product, α-Al_2O_3

Size class in μm	M % mass portion	R% oversize	D% undersize
-63+20	0.22	0.22	100.00
-20+15	0.72	0.94	99.78
-15+10	0.80	1.74	99.06
-10+5	1.90	3.64	98.26
-5+3	3.28	6.92	96.36
-3+2	4.17	11.09	93.08
-2+1	5.71	16.8	88.91
-1+0	83.20	100.00	83.20
Total	100.00	-	-

Investigation of the grain shape factor showed that spherical shape of investigated particles was in the range of 0.55 to 1, the particle size in the range of 0.80 to 40 μm, and the specific surface values was in the range of 20 to 570 m^2/kg, as it shown in the Table 3.

Table 3. Physical characteristics of alumina

Mark of sample	Number of investigated particles	Grain shape factor			Specific surface	Average grain diameter
		min.	max.	average	S, m^2/kg	d_{av}, μm
Intial	203	0.55	1	0.847	20.23	31.80
Alcoa	653	0.55	1	0.993	569.90	1.43
4h/1200^{0}C	686	0.55	1	0.967	188.68	1.39

In all investigated samples, variable parameters are linked with the type and the operation of high-energy mills; induced technological parameters and product characteristics of dry micronized milling are presented in the Tables 4 and 5.

Table 4. Parameters linked with the type of mill, technology and products of dry micronized

Vibrational mill with balls						
Mark of sample	Activ. time t, min	Capacity Q, kg/h	Specific consumption of energy, e, kWh/t	Aver.grain.diam., d_{av}, μm	d_{95}, μm	Portion of α-Al_2O_3, %
Initial	-	-	-	31.18	33.77	20
Alcoa	-	-	-	1.43	16.77	100
1h/1000^{0}C	60	1.00	120	4.78	26.83	44
2h/1200^{0}C	120	0.50	240	3.70	22.86	52
3h/1200^{0}C	180	0.33	360	2.55	18.16	85
4h/1200^{0}C	240	0.25	480	1.39	13.87	90

Table 5. Parameters linked with the type of mill technology and products of dry micronized

Planetary mill with balls						
Mark of sample	Activ. time t, min	Capacity Q, kg/h	Spec. consumption of energy, e, kWh/t	Aver.grain.dim, d_{av}, μm	d_{95}, μm	Portion of α-Al_2O_3, %
Initial	-	-	-	31.18	33.77	20
Alcoa	-	-	-	1.43	16.77	100
1h/1000^{0}C	60	0.50	1100	10.02	52.43	34
2h/1200^{0}C	120	0.25	2200	7.65	51.91	47
3h/1200^{0}C	180	0.16	3430	4.65	36.95	57
4h/1200^{0}C	240	0.12	4400	2.43	22.86	87

Alumina samples were investigated by a method of diffractional analysis, before and after different micronization and heat treatments. In the initial aluminas sample, several phases are presented. Sharp and high diffractional maxima belong to the α-Al_2O_3 phase. A lot of weak and diffused maxima that are often partly overlaped to each other, belong to one or more of so-called "Alumina" phases (ρ, χ, η, γ, κ, θ i δ). According to obtained dif-

fractogrph, θ phase of Al_2O_3 is presented in the initial sample, as it shown in Figure 2.

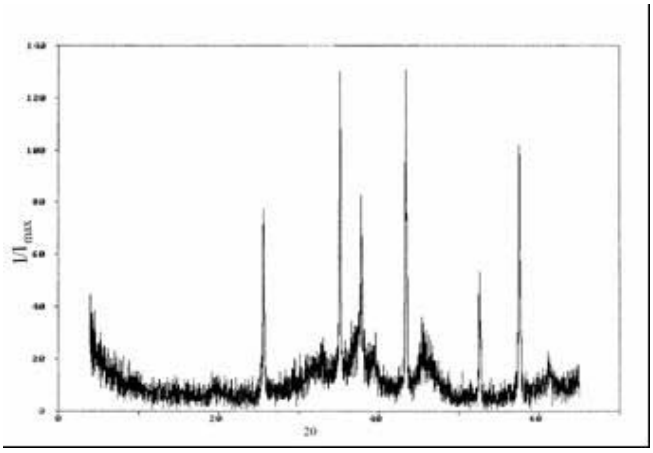

Fig. 2. Diffractional maxima for the initial aluminas sample

By micronization milling of alumina in high-energy vibrational mills for different periods of time (2-4h), and subsequently heat treated at the different temperatures (1000-1200 ^{0}C), quite similar diffractional photographs could be noticed; the diffractographs characterize significant presence of the α-Al_2O_3 phase in comparison with the initial alumina samples (ASTM-cards, 10-173 and 10-425).

With aim to compare experimental results, sample is micronized 4 hours in vibrational mill with balls and than thermally treated at the temperature of 1200 ^{0}C. Difractograph of reference sample-Alcoa is almost identical, (about 90%) with difractograph of reference sample that has sharp and high diffractional maximum (recognized as α-Al_2O_3). That is confirmed also by the literature data (B.C. Lippens, "Structure and Texture of Aluminas", Delft, 1961, ASTM card 10-173, (5) , (Figure 3.). This procedure of transformation γ-Al_2O_3 to α-Al_2O_3 is very efective in dependance on classical method of obtaining crystalline form of α-Al_2O_3 (calcination temperature is over of 1500 ^{0}C).

Diffractographs of the sample activated in vibrational mill and then thermally treated at 1200^{0}C show that desired effects are achieved, Figure 3.

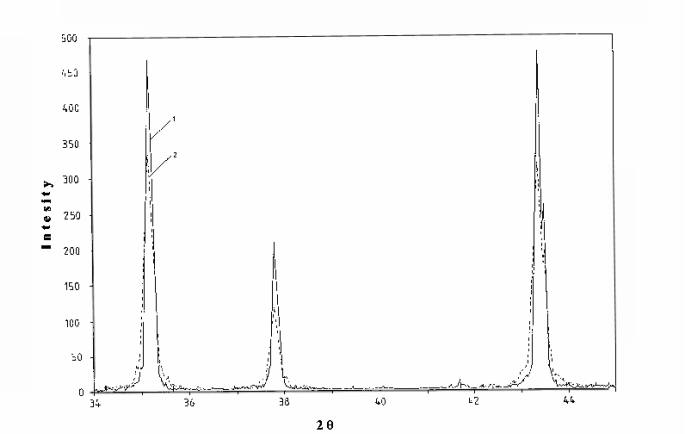

Fig. 3. Diffractional maxima of the reference sample (Alcoa-1) and final product (2) obtained by dry micronization in vibrational mill with balls for 4h

Quantitative participation of the best crystallized α-Al_2O_3 phase in investigated samples was determined by the method of direct X-ray diffracotometry. As a reference used for measuring and calculation of I100 data, certain maximal intensities of the existing pure α-Al_2O_3 component from the "Alcoa" sample were selected. In the Table 6., calculation of quantitative portion of the α-phase in investigated samples is given.

Table 6. The portion of α-Al_2O_3 phase in investigated samples

Mark of sample	d=3.48	d=3.48	d=2.55	d=2.55	Portion of	Lattice parameter		
	I	w	I	w	α-Al_2O_3, %	aÅ	cÅ	VÅ
Initial	102.00	0.35	154.00	0.29	32.00	4.76_1	13.00_1	256.0_6
2h/1000^{0}C	154.00	0.52	234.00	0.44	49.00	4.75_1	12.99_2	254.8_5
2h/1050^{0}C	169.00	0.57	234.00	0.44	54.00	-	-	-
2h/1100^{0}C	253.00	0.86	376.00	0.70	76.00	-	-	-
2h/1150^{0}C	266.00	0.90	433.00	0.81	87.00	4.75_1	12.99_2	254.6_6
4h/1200^{0}C	282.96	0.96	449.00	0.84	90.00	4.74_1	12.98_4	252.9_{14}
Alcoa	295.00	1.00	535.00	1.00	100.00	4.75_1	12.98_4	254.6_{11}

IR spectra of the initial and reference samples as well as the samples micronized in the high-energy vibrational and planetary mills are presented, in the Figures 4, 5, and 6.

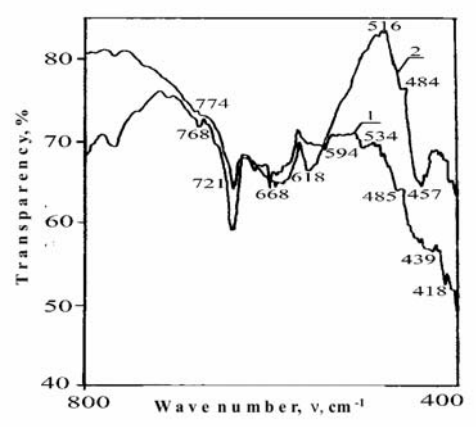

Fig. 4. IR spectra of the initial and reference samples (1-initial sample; 2-reference sample)

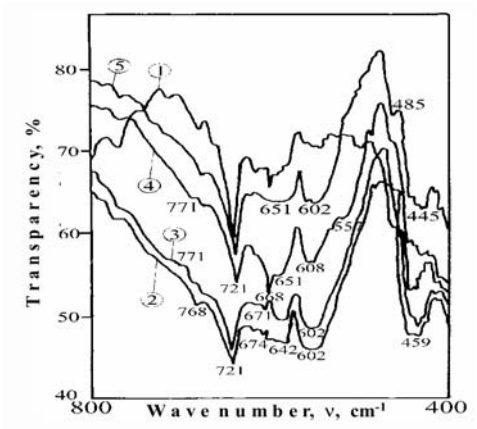

Fig.5. IR spectra of the samples micronized in vibrational mill with balls

Legend:1: the initial sample,
2: the sample with activation of 60 min.,
3: the sample with activation of 120 min.,
4: the sample with activation of 180 min.,
5: the sample with activation of 240 min.

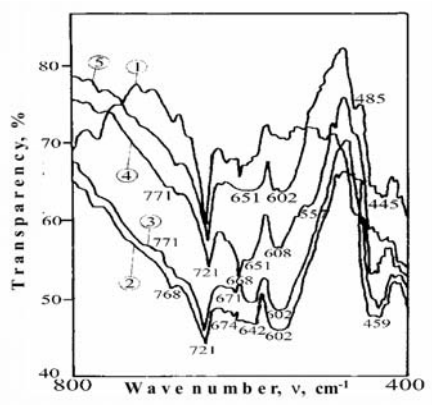

Fig. 6. IR spectra of the samples micronized in planetary mill with balls

Legend:1: the initial sample,
2: the sample with activation of 60 min.,
3: the sample with activation of 120 min.,
4: the sample with activation of 180 min.,
5: the sample with activation of 240 min.

Infrared spectra presented in the Figure 5., and obtained under different conditions of activation in vibrational mill with balls, have a strong absorptional bands that are found at about 720 cm^{-1}. As the micronization and thermal treatment goes on, absorptional bands are reduced, particulary for the sample activated for 60 minutes and then thermally treated at 1000 ^0C. Further reduction of the spectral band width is registered in the region of 510 cm^{-1}.
In the planetary mill with balls, under different conditions of micronization infrared spectra have very strong absorptional bands at about 720 cm^{-1}, reducing with changing the conditions of micronization in the region of extending vibrations at about 600-660 cm^{-1}. As can be seen from the comparative diagrams shown in Figures 5 and 6 infrared spectra are manifested in different forms, which is attributed to the type of mills, time of micronization and calcination temperature.

After the micronization and thermal treatment too, investigations are continued by following actions of experimentally obtained the highest grade quality of Al_2O_3 samples: sintering at 1300 ^0C for 2 hours without micronizа-

tion, sintering at 1300 ^{0}C for 2 hours, and then micronization with time activation of 30 minutes in planetary and vibratory mills, and micronization in planetary and vibratory mill with time activation of 30 minutes and afterwards sintering at 1300 ^{0}C for 2 hours; results of these experiments are identified by electron microscope analysis, given in Figures 7, 8, 9, 10, 11, 12.

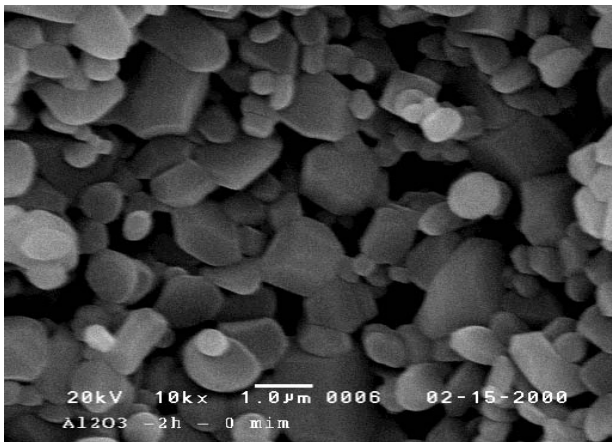

Fig. 7. SEM-α-Al_2O_3 sintered at 1300 ^{0}C for 2 hours without micronization

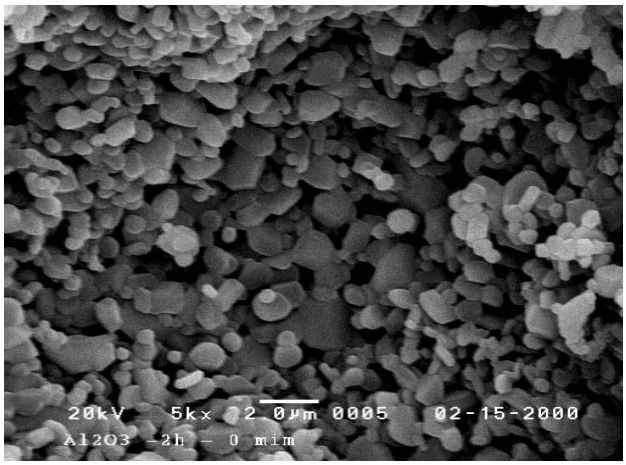

Fig. 8. SEM-α-Al_2O_3 sintered at 1300 ^{0}C for 2 hours with micronization

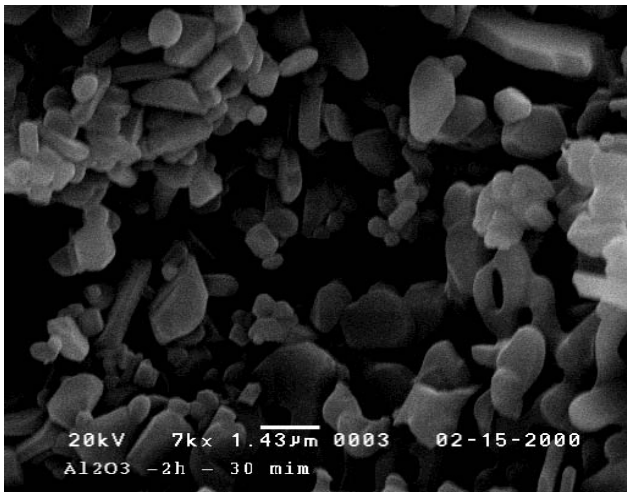

Fig. 9. SEM-α-Al_2O_3 sintered at 1300 ^{0}C for 2 hours with micronizat ion then micronized for 30 minute in planetary mill

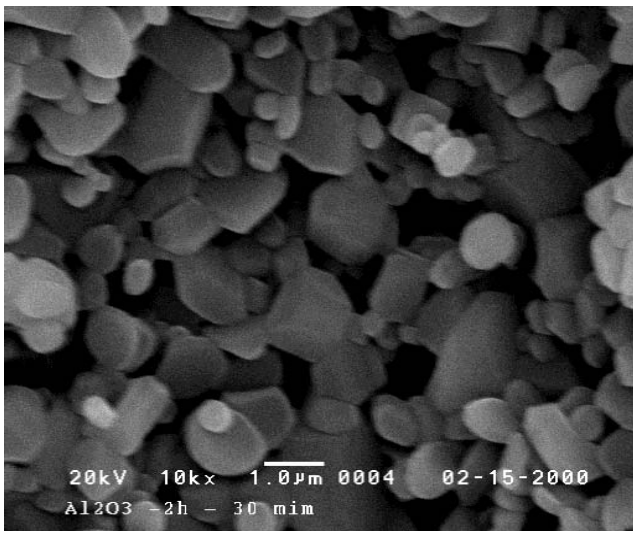

Fig. 10. SEM-α-Al_2O_3 sintered at 1300 ^{0}C for 2 hours with micronizat ion then micronized for 30 minute in vibratory mill

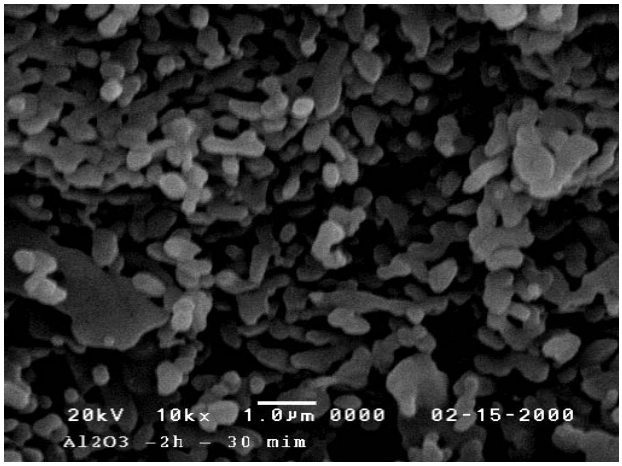

Fig. 11. SEM-α-Al_2O_3 micronized 30 minute in planetary mill and then sintered at 1300 ^{0}C

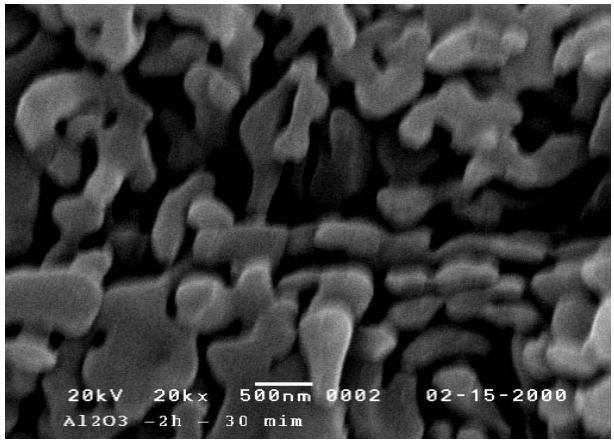

Fig. 12. SEM-α-Al_2O_3 micronized 30 minute in vibratory mill and then sintered at 1300 ^{0}C

4. Conclusions

On the basis of theoretical knowledge, the complex experimental investigation of the alumina micronized enabled:

- determination of the basic characteristics of product (grain size composition, grain shape, specific surface, etc.),

- determination of kinetic parameters of high-energy mills during activation because their change causes certain structural defects and change of the alumina reactional capacity,

- determination of the surface energy changes, unit cell parameters and degree of the phase transformation,

- to define and control reactional, structural and rheological changes by combined of both micronization and heat treatment, (grain size and grain shape) of the initial and final products.

Described operations of high-energy mills in the process of the alumina micronization have many advantageous in dependance on the usual ones. First of all, size, shape and specific surface of particles can be controlled by duration of micronization treatment. The second advantage is the possibility to obtain well crystallized α-Al_2O_3 at lower temperature (1200 ^{0}C), in comparison to the usual one (over 1500 ^{0}C), thus making the production process much cheaper.

5. References

1. N. Magdalinovic: Grinding and Classification of the Mineral Raw Materials, Belgrade, Yugoslavia, (1991).

2. K. Wefers, C. Micra: Alcoa Technucal paper N0 19, Revised, Alcoa laboratories, Pittsburg, P. A., USA, (1987).

3. Ljubisa Andric: "Mechanochemical activation of alumina and its influences on change of the alumina crystal structure", Ph.D. Thesis, University Belgrade, Yugoslavia, (1999).

4. Ljubisa Andric, Deana Zivanovic, Sinisa Milosevic: Change of the physical-chemical characteristics of the materials by mechanical activation" Advance Science and Technology of Sintering, New York, USA, Plenum Press, pp. 187-192., (1999).

5. B.C. Lippens: "Structure and Texture of Aluminas", delft, (ASTM-cards), (1961).

6. V. Molchanov, O. Selezneva, E. Zhirov: Aktivacya mineralov pri izmelchenii, Nedra Moskow Russia, pp. 52-60, (1988).