ALUMINA TECHNOLOGY IN ZHENGZHOU LIGHT METAL RESEARCH INSTITUTE (ZLMRI) OF CHINA

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ABSTRACT

Three entries of alumina technique which has been developed successfully in ZLMRI are briefed: (A) tube heating-autoclave digestion for diasporic bauxite; (B) two-stage precipitation for sandy alumina at high caustic concentration. (C)production of low soda alumina. In ZLMRI, the pilot tests for processing PINGGUO and HENAN diasporic bauxite have been carried out and under the conditions of digestion temperature: 260-275 °C, heating time: 10-12 min., heating preservation time: 25-40 min., liquor concentration Na_2O_c: 160-230 g/l, molar ratio (α_K=Na_2O/Al_2O_3): 1.45-1.55, alumina relative yield (η_r) was larger than 92 %. It was demonstrated that the energy consumption for processing diasporic bauxite by the intensive digestion at high temperature could be reduced to 3500 Mcal/t-Al_2O_3; the most effective device of intensive digestion is the tube heating-autoclave digester. In ZLMRI, a pilot test to produce sandy alumina from a high concentration sodium aluminate solution (Na_2O_c: 155 g/l, α_K: 1.55) with a flow rate of 6.5 m^3/h also was organized. The yield of alumina was 73.7kg/m^3, with its particle size of 0.2 % for +100 mesh, and 7.3 % for -320 mesh, attrition index of 24.2 % and specific surface area of 63.8m^2/g. Using aluminum hydroxide which is made in ZLMRI, by adopting special addition agents and special process treatment, ZL-series low soda alumina which has crushability and high sintering activity has been produced. ZL-Aluminas have high chemical purity (Al_2O_3: 99.7 - 99.8 %) low residual soda content (Na_2O: 0.14-0.06 %), high density (3.96-3.97 g/cm^3), and high melting point (2040° C).

1. INTRODUCTION

Bauxite resources are abundant in China (ascertained reserves are 1.16 Gt, they occupy the eighth place in the world), but most of them are middle or low grade diasporic bauxite with high contents of both alumina and silica,they are difficult to digest. China has produced alumina from diasporic bauxite for more than 30 years , but direct heating digestion technique by steam is still used in Bayer process. In this case, digestion temperature is low, the liquor concentration is high, and long digestion time is needed . So it causes lower extraction efficiency and much

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higher energy consumption than that of advanced technology.

So since 1975 at ZLMRI, a new intensive digestion technique by tube digester and tube heating - autoclave digester has been developed and an alumina pilot plant on the basis of this technique with slurry flow of 4-12 m^3/h was built in 1987 at ZLMRI. Then pilot tests for intensive digestion of diasporic bauxite were carried out.

As is known to all, the strategic principle to give priority to developing aluminum industry is carrying out in China. In order to meet the needs of newly built electrolytic aluminum plant with large-scale prebake anode electrolytic cell and dry purification of fluegas,and also to provide technologic parameters of reducing energy consumption for built alumina plant, a pilot-plant-scale production test for sandy alumina from high concentration sodium aluminate solution(Na_2O_c155g/l, α_K1.55)by two-stage precipitation was carried out.

Studying on alumina of non-metallurgic use has being attached importance in ZLMRI. Recently, using aluminum hydroxide made in Alumina Pilot Plant of ZLMRI as starting materials,by adopting of special addition agents and special treatment process, ZL-series low soda alumina has been produced.

In this paper, authors briefly describe the three entries of the alumina technique above mentioned which have been developed successfully in ZLMRI of China.

2. INTENSIVE DIGESTION TECHNIQUE FOR DIASPORIC BAUXITE BY TUBE HEATING - AUTOCLAVE DIGESTER [1]

2.1. Digestibility of diasporic bauxite

In order to achieve high digestion yield and economic efficiency , intensive digestion has been carried out in many alumina plants for either trihydrate or monohydrate types of bauxite at high temperature. The present applied digestion temperature is higher by about 40°C than the previous digestion temperature for both gibbsitic bauxite and boehmitic bauxite. But in fact it is not applied in the digestion of diasporic bauxite, because of many difficulties on the technology and high cost in the design and in the manufacture of high temperature autoclave (above 260 °C). In 1960's a tube digestion technology was developed and applied by VAM. The tube digestion temperature of digester could reach 280-300 °C. It gave applicable possibility for the intensive digestion of diasporic bauxite.

Our experiments have proved when the digestion temperature of diasporic bauxite was increased above 280 °C, that the alumina extraction efficiency increased considerably (see Fig.1), the digestion rate was accelerated obviously, and that the effect of caustic soda concentration upon alumina yield was minimized(as show in Fig.2 and Table 1).

2.2 Energy consumption of alumina production with diasporic bauxite

According to the data of Lange,the dissolution heat of gibbsite is increased with temperature,and it is 200kcal/kg-Al_2O_3 at Bayer digestion temperature(145°C).But the dissolution heat of diaspore under its own digestion condition (the temperature ranges from

Table 1. The Alumina Digestion Efficiency as Function of the Digestion Time , Liquor Concentration and Temperature

Concentration Na_2O_c(g/l)	digestion Temp. (°C)	digestion time (mine.)	Alumina efficiency (%)
140	280	15	89.1
160	280	15	89.5
200	280	15	90.3
225	245	90	84.4

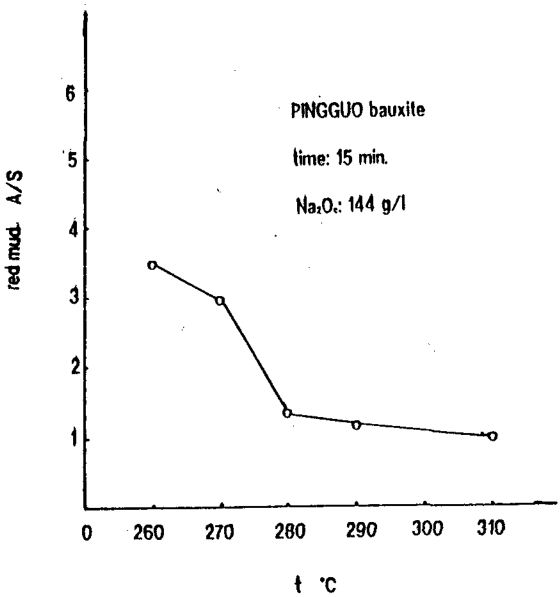


Fig.1 Relation between Digestion Temperature and Al_2O_3/SiO_2 of Red Mud

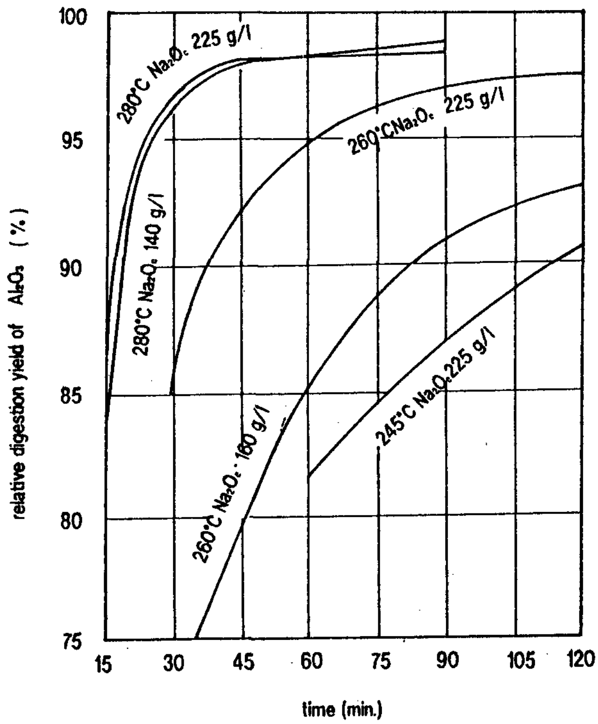


Fig.2 Digestion Time, Temp. and Na_2O_c vs. Relative Digestion Yield of Alumina

250°C to 300°C)is about 143 kcal/kg-Al_2O_3, and lower than that of gibbsite under their industrial digestion conditions. But digestion of diasporic bauxite has some disadvantages at high temperature. For example, temperature difference between digested slurry and surrounding is comparatively large, and most of heat will be lost. This heat has to be recovered and utilized. So effective measures have to be taken, including increment of heat insulation during digestion process, and using (1)multiple-stage flash tanks to reduce the temperature and pressure of the slurry and to preheat the slurry with flashed steam,(2)intensive digestion of high temperature to decrease the caustic soda concentration of the liquor to 140-160 g/l, and(3)high concentration of precipitation pregnant aluminate solution (about 150 g/l) to reduce the concentration difference between digestion and precipitation operations and to reduce the heat consumption by the way of reducing evaporation of water.

The energy consumption of treating Chinese diasporic bauxite (Al_2O_3 70 %, SiO_2 6.4 %, Fe_2O_3 4 %) will be reduced, when above mentioned measures are employed. The calculated data of heat consumption for processing diasporic bauxite are as follows:

heat for preheating slurry	305.5	Mcal/t-Al_2O_3
heat for digestion	851.0	Mcal/t-Al_2O_3
heat for evaporation	151.0	Mcal/t-Al_2O_3
heat for calcination	750.0	Mcal/t-Al_2O_3
electricity(300kWH/t-Al_2O_3)	855.0	Mcal/t-Al_2O_3
total	2912.5	Mcal/t-Al_2O_3

As a conclusion, the practical energy consumption of processing diasporic bauxite by Bayer process is not high, it can be less than 3500Mcal /t-Al_2O_3, including some other unpredictable heat losses. It is in the same level as that of processing gibbsitic and/or boehmitic bauxite.

At present the autoclaves, in which slurry is heated directly by steam, are still used for digesting diasporic bauxite in few countries. This kind of digester consumes twice more energy than that of advanced digester. Comparison of the energy consumption between intensive digestion and current digestion is shown in Fig.3.

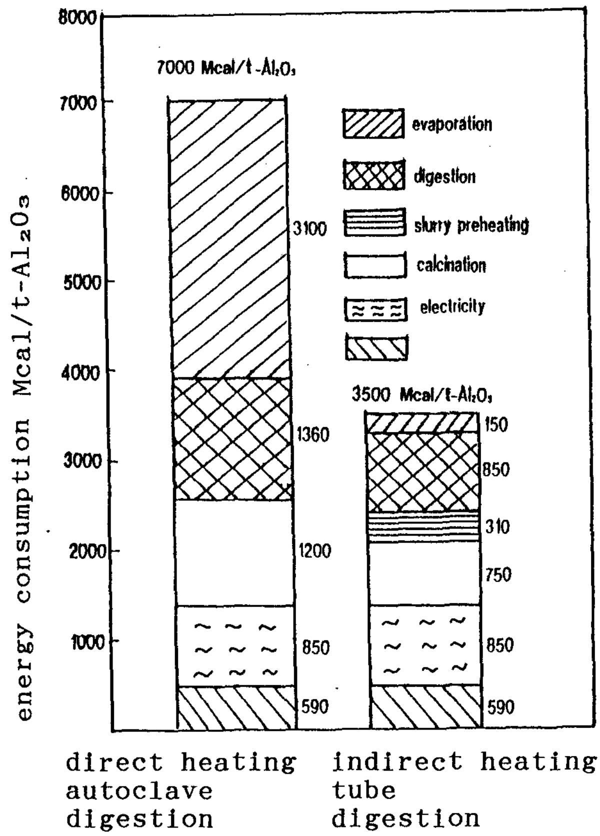


Fig.3 Comparison of the Energy Consumption between Directly Heating Digestion by Stream and Indirectly Heating Digestion by Inorganic Salts

2.3 development of intensive digestion technique of diasporic bauxite.

In order to decrease the energy consumption as much as about 50% (3500 Mcal/t-Al_2O_3), we have developed an intensive digestion technique of Bayer process by tube heating - autoclave digester and tube digester at above 260°C for Chinese diasporic bauxite. During 1975-1982, in ZLMRI a set of tube digester and tube heating-autoclave digester was installed. Three types of reactors were tested. On the basis of the test results, digestion technology for Pingguo bauxite which is very difficult to digest was studied. It was obtained from our experiments that the alumina relative digestion yield could reach 91-93% under the conditions of 135-140g/l caustic soda liquor concentration, 290°C digestion temperature and 12 minutes time with the tube digester. The yield of 96-98 % had been reached under the conditions of 140 g/l Na_2O_c concentration , 260 °C digestion temperature and 30-60 minutes time with the tube heating - autoclave digester[2].

In 1987, ZLMRI built up an alumina pilot plant with slurry flow of 4-12 m^3/hr which is a full flow plant from ore crushing to the production of aluminum hydroxide. The digestion temperature in tube digester can reach 300 °C, and the digestion temperature in tube-heating autoclave digester can reach 280 °C. The pilot tests for processing Pingguo and Henan bauxite to produce aluminium hydroxide have been carried out for more than two years. It was provided that we have made three technical breakthroughs: scaling at tube, equipment wearability and alumina yield, which used to be considered as hard-to-overcome difficulties in the treatment of Chinese diasporic bauxite with tube digester. It was also provided that tube-heating autoclave digester is effective for treating Chinese diasporic bauxite, and it has the advantages of both tube digester and autoclaves. The test results are shown in Table 2.

Table 2. Test Results of Diasporic Bauxite Digestion

	PINGUO bauxite	HENAN bauxite	
		A	B
Digestion temp.(°C)	260-265	260-265	270-275
Heating time (min.)	12	10 - 12	10 - 12
Heating preservation time (min.)	40	25	25
Liquor concentration Na_2O_c (g/l)	220-230	190-220	160-180
Molar ratio α_k Al_2O_3/SiO_2	1.50-1.55	1.50-1.55	1.45-1.55
Alumina relative yield	> 92 %	> 94 %	> 95 %

It was demonstrated by our pilot tests that the intensive digestion of high temperature is very effective on energy saving for processing diasporic bauxite. The energy consumption for processing diasporic bauxite can be reduced to 3500 Mcal/t-Al_2O_3 by intensive digestion. It is almost the same as processing gibbsitic and boehmitic bauxites. At present the most effective intensive digestion device is tube-heating autoclave digester. It will be widely used to process diasporic and boehmitic bauxite in the near future.

3. PRODUCTION OF SANDY ALUMINA FROM HIGH CONCENTRATION SODIUM ALUMINATE SOLUTION BY TWO-STAGE PRECIPITATION [3]

3.1 Technologic process

For production of sandy alumina,two-stage precipitation process was been tested. First stage is the agglomerative stage, in which fine particles agglomerate and become big particles. Second stage is the cohesion growth stage, in which agglomerated particles further cohere, grow, and become strongly. The frowchart is shown in Fig. 4. The fine seed of aluminum hydroxide was added to high concentration sodium aluminate solution, which was passed through the precipitation tanks of agglomerative stage and vacuum chiller then. Cooled slurry, to which added coarse seeds of aluminum hydroxide, goes to the precipitation tanks ofcohesion growth stage. Precipitated slurry was passed through classificator. The fine particles of aluminum hydroxide contained in overflow through pressfilter go back as fine seed. The aluminum hydroxide of middling size contained in middle-flow through vacuum filter goes back to the circuit as coarse seed. The underflow passed through vacuum filter and became aluminum hydroxide product, it was washed by hot water, calcined by calciner, and became sandy alumina product.

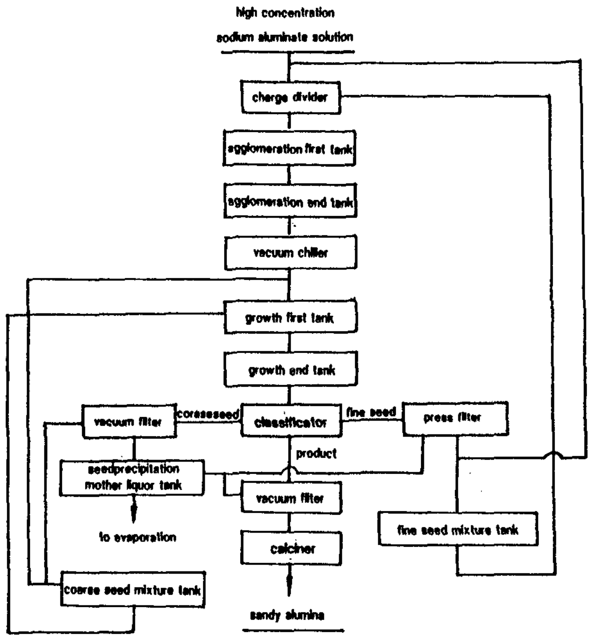


Fig.4 Flowchart of Sandy Alumina Production by Two-stage Precipitation

3.2 Main equipments

3.2.1 Precipitation tank:

Φ 3x11.7m, efficient volume 63 m^3, with air stirrer and steam casing pipes for regulation temperature of the tanks , use for both the agglomeration tanks and the growth tanks.

3.2.2 Revolving drum vacuum filter: filter area is $2m^2$/set,use as filtering of $Al(OH)_3$ coarse seed of middle size and $Al(OH)_3$ product.

3.2.3 Auto frame filter-press:
filter area 15 m^2/set, use for filtering of $Al(OH)_3$ fine seed.

3.2.4 Calciner: Φ 0.6 x 5 m, inside diameter 0.3m, slope 3 %, 1-1.8 rpm, light diesel as fuel, with cyclone.

3.3 Precipitation test

3.3.1 Precipitation process conditions

The components of high concentration sodium aluminate solution were:TNa_2O166.7 g/l, $Al_2O_3$164.2 g/l, Na_2O_c154.7 g/l, and α_k1.55. Form ten sets of precipitation tanks into a group, the parts were agglomeration stage, the others were cohesion growth stage. Total retention time for ten sets of tanks was 75 hours.The temperature of agglomeration first tank was 73.1°C, the temperature of end tank was 70.9°C.The temperature of cohesion growth first tank was 61.4°C, the temperature of end tank was 48.6°C. Fine seed coefficient was 0.23. Content of fine seed $Al(OH)_3$ was 36.3 % for -320 mesh. Coarse seed coefficient was 1.22. Content of coarse seed $Al(OH)_3$ was 15.5 % for -320 mesh. Weighted average contents of fine seed and coarse seed were 18.8% for -320 mesh. The flow of high concentration sodium aluminate solution was 6.4 m^3/hr.

3.3.2 Main results of the tests

3.3.2.1 Alumina yield of sodium aluminate solution

The components of precipitation mother liquor were: Na_2O_c 160.6

g/l, Al_2O_3 93.7 g/l; α_K 2.82 ; precipitation rate was 45 %, alumina yield of the solution was 73.7 kg/m^3.

3.3.2.2 Contents of aluminum hydroxide product

They were 0.3 % for +100 mesh, 58.5 % for -100+200 mesh, 33.3 % for -200+320 mesh, 7.9 % for -320 mesh.

3.3.2.3 Contents and intensity of alumina product

Contents of alumina obtained from follow-up calciner by a small alumina pipe rotary kiln with Φ 60x1200mm at 1080°C were 0.1 % for +100 mesh,56.4% for -100+200 mesh, 34.6% for -200+320 mesh, 8.9 % for -320 mesh. The attrition index of alumina was 24.8 %.

3.3.2.4 Agglomeration coefficients

They were 33.1 % for first tank, 44.0 % for end tank.

3.3.3 Control and regulation of size balance For balanced production, the balance of particles size must be ensured. Our main experiences for control and regulation of particles size balance in precipitation system are adjusting amount and size of $Al(OH)_3$ fine seed at proper time and adjusting temperature of agglomeration first tank and growth first tank, if necessary.

3.3.4 Agglomeration of aluminum hydroxide fine particles

It is considered that agglomeration basically occurs in the fine particles below 20μ m. For achieving efficient agglomeration small seed coefficient, proper stirring and retention time must be selected. The formula of agglomeration efficiency(D,%) used by us was:

$$D = (A - B) \times 100 \% / A$$

A - the content of fine seed $Al(OH)_3$, % for -320 mesh

B - the content of agglomeration product $Al(OH)_3$,% for -320 mesh

Our tests demonstrated: (1)precipitation tank with air strirrer was applicable for agglomeration; (2) fine seed $Al(OH)_3$ obtained from sodium aluminate solution had enough activity without washing, it was applicable for agglomeration operation with high efficiency.(3)when the size of fine seed varied in certain range, all of them obtained high agglomeration efficiency.

3.3.5 Classification of aluminum hydroxide

We used a new type of classificator for the classification of aluminum hydroxide. By one set of the classificator, coarse seed, fine seed, and product aluminum hydroxide can be obtained in the same time, i.e. the overflow was $Al(OH)_3$ which contained more of fine particles, it was applicable for using as fine seed; the middle-flow was $Al(OH)_3$ which contained less of fine particles,it was applicable for using as coarse seed; the underflow was $Al(OH)_3$ product which contained few fine particles. The classificator can obtained high classification efficiency for different charge size and can be operated readily.

3.3.6 Vacuum cooling

In order to increase the oversaturability of sodium aluminate solution and the intensity of $Al(OH)_3$, the temperature of $Al(OH)_3$ slurry from agglomeration stage must be lowered before it goes to growth stage. We used a vacuum chiller, neednot worry about scaling of $Al(OH)_3$. The vacuum must be 650 - 700 mm Hg.

3.4 Calcination of aluminum hydroxide

For calcination of $Al(OH)_3$, a calciner(3.2.4) was used. The temperature of the calciner was regulated according to that specific surface area of alumina product was in 45 - 65 m^2/g.

The main properties of calcined sandy alumina were as follows:

size: 0.2 % for +100 mesh
7.3 % for -320 mesh
content of α - Al2O3: 7.3 %
LOI(300 - 1100°C): 0.78 %
tap density: 1.08 g/cm^3
contents of impurities: SiO_2 0.01-0.02 %
Fe_2O_3 0.020-0.024 %
Na_2O 0.34-0.35 %

attrition index: 24.2 %
specific surface area: 63.8 m^2/g
angle of repose: 31°30'
bulk density: 0.90 g/cm^3
true density: 3.41 g/cm^3

4. PRODUCTION OF LOW SODA ALUMINA

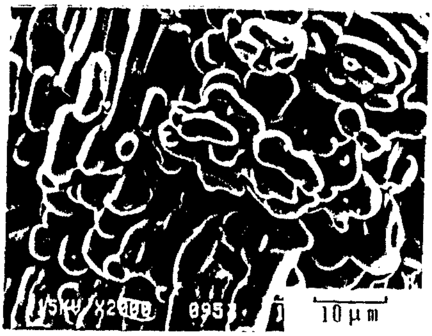
Using aluminum hydroxite made in Alumina Pilot Plant of ZLMRI, by adopting of some special addition agents and special process ZL-series low soda alumina has been produced. By comparison with conventional α - Al_2O_3, ZL-Aluminas have excellent properties as follows(see Table 3 and Fig. 5):

(1) good crushability: by wet crushing with alumina ball mill for 24-32 hours, it can be crushed to size of 3.0 - 1.5μ m.
(2) high sintering activity: sintering temperature is lower by 50-80°C than that of conventional alumina .
(3) high chemical purity: Al_2O_3 99.7-99.8 % .
(4) low residual soda content: Na_2O 0.14-0.06 %.
(5) high density: true density 3.96-3.97 g/cm^3.
(6) high melting point: about 2040°C.
(7) ceramics products made from ZL-Aluminas have good thermal conductivity and heat-shock resistance, and high electrical resistivity at room and elevated temperature.

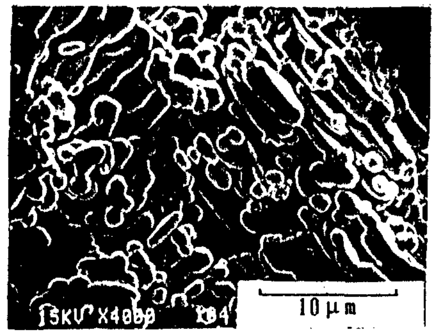
Table 3. Characteristics of ZL-Aluminas

Typical chemical analysis weight percent(%)	ZL-Aluminas ZL-1	ZL-10	ZL-20	ZL-30
Al_2O_3	99.6	99.7	99.7	99.7
Na_2O	0.14	0.06	0.06	0.06
SiO_2	0.03	0.03	0.04	0.04
Fe_2O_3	0.03	0.03	0.03	0.03
MgO	0.01	0.01	0.01	0.01
B_2O_3	0.05	-	-	-
LOI(300-1100°C)	0.05	0.03	0.03	0.03
Typical physical properties				
True density(g/cm^3)	3.96+	3.97+	3.97	3.97
Bulk density(g/cm^3)	0.8-0.9	0.8-0.9	0.7-0.8	0.7-0.8
Particles size(μ m)	30-60	30-60	30-60	30-60
Ultimate crystal size(μ m)	3-5	1-3	1-3	0.3-1
Ground particle size Sedigraph median*(μ m)	1.92	1.72	1.44	1.05
Grinding time, hrs.	10	10	6	10

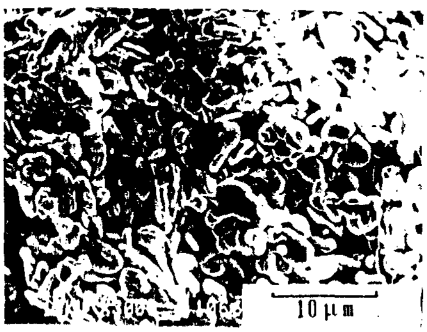
* Grinding conditions: 500g Al_2O_3, 2000g 20-25 diameter media, 2 L ball mill at 90 rpm.



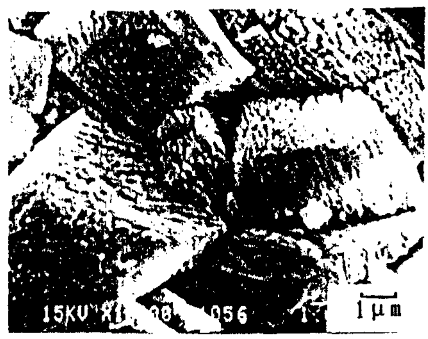
ZL-1 SEM X2000



ZL-10 SEM X4000



ZL-20 SEM X3000



ZL-30 SEM X10000

Fig.5 Scanning Electron Micrographs of Unground ZL-Aluminas

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