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INFLUENCE OF CHLORIDE IONS ON CRYSTAL GROWTH OF CORUNDUM DURING CALCINATION OF HYDRARGILLITE

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Abstract. The essential technological parameters of alumina obtained by calcination of hydrargillite are the habit, size and the structure of corundum crystals. Earlier studies have shown that mineralizing additions can lower considerably the temperature of phase conversions $\gamma \rightarrow \delta \rightarrow \Theta \rightarrow \alpha\text{-Al}_2\text{O}_3$.

The paper presents the results of investigations of the process of calcination of hydrargillite in the presence of chloride ions introduced as aluminium oxychloride, $\text{AlOCl} \cdot n\text{H}_2\text{O}$. The latter was selected as the most suitable mineralizer which allows obtaining 98—100% conversion of hydrargillite into corundum already at 1523 K.

The resulting corundum crystals form as pseudomorphic aggregates that replace hydrargillite grains and are characterized by close packing of the constituent grains. The elementary crystals have a platytabular habit and are less than 3 μm in size. It has been found that the process of calcination presumably involves diffusion.

INTRODUCTION

According to Dereń et al. (1975), experimental results of Evans indicate that in a number of conversions hydrargillite — transient phases — corundum, corundum forms at 1373—1473 K. Maczura et al. (1975) state that a complete transition occurs at 1473—1573 K. However, to obtain corundum crystals of 2 μm in size, the required temperature amounts to 1773 K, and 1930 K is necessary to obtain crystals of 2.5 μm .

Physical and chemical properties of aluminium hydroxide, as well as the parameters of calcination process, determine the degree of conversion into corundum, the size and shape of aggregates being formed, as well as the dimensions and crystal habit of elementary grains in an aggregate.

Calcination of aluminium hydroxide applied in industrial processes produces the so-called technical alumina in which corundum content varies from 25 to 88% (Gibas, 1971). According to Clark and White (1950),

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the re-calcination process carried out to change the rest of alumina into corundum requires much more energy than single calcination of aluminium hydroxide conducted under specially chosen conditions. In order to expedite the seeding and growth of corundum crystals, different kinds of agents are used. They are introduced into aluminium hydroxide before or during the process of calcination. Generally, to avoid contamination of the final product, alumina salts or salts that decompose at lower temperatures are added. The anion formed during the decomposition reacts with aluminium (NH_4F , NH_4Cl).

Many authors (Hlavač and Matousek, 1970; Rutman et al., 1978) report the strong mineralizing effect of aluminium fluoride on the degree of transformation: Al-hydroxide — transient phases — corundum. These authors point out that aluminium fluoride added to hydroxide speeds up the dehydration of hydroxide, decreases the temperature of conversion into corundum, and accelerates the corundum crystal growth. The narrow range of temperatures (1173—1273 K) at which the complete transformation into corundum proceeds, hinders the size control of grains being formed. Consequently, corundum mineralized by aluminium fluoride and manufactured on an industrial scale is characterized by the large scatter of grain dimensions and large sizes of grains. It is feasible that this undesirable scatter of grain dimensions is caused by heterogeneous distribution of aluminium fluoride introduced into the process in solid state.

Searching for a more convenient mineralizer, it was assumed that it should be water-soluble, it should decompose at temperatures higher than the decomposition temperatures of hydrargillite and should not crystallize during the drying process. After decomposition it should remain in the amorphous state and change into corundum at as low temperatures as possible. The homogeneity of mineralizer distribution should influence the crystal habit and size of grains, as well as the grain distribution of the final product. The survey of data referring to the decomposition of aluminium salts and to their behaviour during the dehydration process has shown that those specific requirements are met by aluminium chloride and aluminium polyoxychloride.

According to Funaki and Shimuzu (1959), aluminium chloride decomposes to an amorphous product at temperatures ranging from 773 to 973 K, and this product changes into corundum during further heating ($\gamma \rightarrow \delta \rightarrow \theta \rightarrow \alpha \cdot \text{Al}_2\text{O}_3$). In accordance with the given sequence, Stirland et al. (1958) have proved that the decomposition products of hydrated aluminium chloride convert into corundum at 1373 K. Schäfer et al. (1950) and Ischerwood (1970) have shown that aluminium oxychloride behaves in a similar way during heating.

This paper presents results of studies of the mineralizing effect of aluminium oxychloride on the conversion degree of hydroxide into corundum and on the morphological structure of the obtained corundum.

EXPERIMENTAL MATERIAL

- a. Aluminium hydroxide — Hungarian; X-ray techniques showed hydrargillite content only.
- b. Technical alumina — Hungarian; containing 40% of corundum.
- c. Aluminium salt of $\text{AlOCl} \cdot n\text{H}_2\text{O}$ group — obtained in the labora-

tory. This preparation is characteristic for its conversion into vitreous state during dehydration process, without losing re-solubility.

d. Corundum obtained from aluminium hydroxide mineralized with aluminium fluoride; calcination temperature 1500K.

PREPARATION OF POWDERS AND CALCINATION PROCESS

Aluminium hydroxide and technical alumina have been wetted with aluminium oxychloride. The samples with added mineralizer have been subjected to heat treatment in a laboratory crucible furnace at 1523K. Initial alumina hydroxide has been re-calcinated for comparison.

METHODS OF INVESTIGATIONS

The degree of conversion of the samples into corundum has been determined by X-ray methods and by pycnometer measurements of powder density. The specific surface area has been determined by Nelson's and Eggertson's methods. The mean equivalent diameter has been calculated from measurements of the specific surface area and density, as well as from the grain distribution evaluated by Andreasen's method. Sodium and potassium contents have been determined spectrophotometrically.

The crystal habit, the degree of aggregation and the shape of aggregates have been determined with a JEOL scanning microscope.

RESULTS AND DISCUSSION

An analysis of the results (Table 1) indicates that at 1523K the introduced addition allows obtaining a product that contains 98—100% of corundum. The degree of conversion into corundum and the adequate density for the sample mineralized with aluminium oxychloride (3, Tab. 1) are similar to those in the sample mineralized with aluminium fluoride (4, Tab. 1). The grain distribution, specific surface area and the calculated equivalent diameters appear to be more interesting for the oxide mineralized with oxychloride.

A comparison of the grain mean equivalent diameters calculated from the specific surface areas and from the grain distribution indicates the occurrence of aggregates in the samples. This is in agreement with microscopic observations (Phot. 1—16).

It is worth noting that single calcination of aluminium hydroxide without any additions gives a product similar to one obtained by recalcination of technical alumina with a mineralizer in respect of the degree of conversion, density and the specific surface area (2 and 6, Tab. 1). This fact confirms the experimental results of Clark and White (1950), who have found that an Al-oxide decreases its conversion capability into corundum when the calcination process is not carried out in one stage. It will be noticed that in comparison with the initial raw material, sodium

Table 1
Physicochemical properties of raw materials and calcinated products

No	Kind of samples	Content of α -Al ₂ O ₃ (%)	Density (kG/m ³)	Specific surface area (m ² /G)	Calculated equivalent diameter		Content of	
					S* (μ m)	A* (μ m)	Na ₂ O (%)	K ₂ O (%)
1	Aluminium hydroxide (Phot. 1—3)	0	2341	7.4	0.34	5	0.132	0.007
2	Aluminium hydroxide calcinated at 1523 K	86—90	3909	6.77	0.22	1.5	0.124	0.003
3	Sample 1 with addition of oxychloride, calcinated at 1523 K (Phot. 4—7)	98—100	3975	1.86	0.31	2.55	0.065	0.0023
4	Aluminium hydroxide mineralized with aluminium fluoride, calcinated at 1500 K (Phot. 14—16)	ca 98	3974	1	ca 2	17	0.103	0.0021
5	Technical alumina (Phot. 10—13)	ca 40	3678	23.7	0.068		not determined	
6	Sample 5 with oxychloride added, calcinated at 1523 K	90—93	3914	7.63	0.2	1.3	not determined	

* S — from specific surface area, A — by Andreasens method.

content in the sample mineralized with oxychloride decreases (1, 2 and 3, Tab. 1).

Microscopical observations reveal significant morphological differences between the investigated samples. These differences concern not only the shape and content of aggregates and the orientation of elementary grains but also the size and degree of the growing crystals forming these aggregates. The visible fractures and the large amount of small grains, either randomly distributed at the surface or oriented in a more ordered manner in the direction of the alumina hydroxide grain centre (Phot. 1—3), may be the result of the conditions of preparation of the samples. The vacuum conditions in the SEM chamber might have led to partial decomposition of a grain when fractures could have enabled relaxation of the created stresses.

In case of the samples mineralized with oxychloride (Phot. 4—7, 10—13), the shape of aggregates, as well as the direction of elementary grain orientation in an aggregate, is preserved. Plate-shaped grains are indicative of the diffusive mechanism of calcination of corundum seeds after the hydroxide grain decomposition in layers. The pseudomorphic nature of the aggregates reduces the dispersion of elementary grain dimensions in an aggregate.

Noticeable changes in the aggregate shapes, the crystal habit of their grains, as well as their mutual orientation, occur in the oxide mineralized with aluminium fluoride (Phot. 14—16). They are characterized by the angularity of grain shapes, much larger sizes and the scatter of grain dimensions when compared with grains formed in the presence of aluminium oxychloride. The crystal habit of those grains resembles that of crystals formed during crystallization from solutions and alloys of low viscosity.

SUMMARY

The above investigations have shown the positive influence of mineralizing water-soluble additions containing chloride ions on the uniform growth of corundum crystals formed as pseudomorphic aggregates which replace the crystals of initial hydrargillite.

The application of the above-mentioned mineralizer allows obtaining 90—100% conversion of hydrargillite into corundum already at 1530K. Average sizes of the elementary crystal grains in an aggregate amount to 3 μ m.

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WPLYW JONÓW CHLORKOWYCH NA WZROST KRYSZTAŁÓW KORUNDU PODCZĄS KALCYNACJI HYDRARGILLITU

Streszczenie

Istotnym parametrem technologicznym tlenku glinu otrzymywanego przez kalcynację fazy hydrargillitowej jest pokrój, rozmiary i struktura kryształów korundu $\alpha\text{-Al}_2\text{O}_3$. Stwierdzono we wcześniejszych badaniach, że dodatki mineralizujące mogą znacznie obniżyć temperaturę przekształceń fazowych $\gamma \rightarrow \delta \rightarrow \theta \rightarrow \alpha\text{-Al}_2\text{O}_3$.

W pracy przedstawiono wyniki badań procesu kalcynacji hydrargillitu w obecności jonów chlorkowych wprowadzanych pod postacią tlenochloru glinu $\text{AlOCl} \cdot n\text{H}_2\text{O}$ wytypowanego jako najbardziej przydatny mineralizator, pozwalający już w temperaturze 1523 K uzyskać 98–100% przekształceń hydrargillitu w korund. Otrzymywane kryształy korundu powstają jako pseudomorficzne agregaty zastępujące ziarna hydrargillitu i charakteryzują się gęstym upakowaniem kryształów wchodzących w skład agregatu. Elementarne kryształy składowe mają pokrój płytkowy i wielkość $< 3 \mu\text{m}$. Stwierdzono prawdopodobieństwo dyfuzyjnego mechanizmu procesu kalcynacji.

OBJAŚNIENIA FOTOGRAFII

Plansza I

Fot. 1–3. Ziarna wodorotlenku glinu uzyskanego w procesie Bayera:

- 1 — mono- i polikryształy $\text{Al}(\text{OH})_3$, SEM, 200×,
- 2 — monokryształ $\text{Al}(\text{OH})_3$ o pokroju heksagonalnym, SEM, 1000×,
- 3 — budowa agregatowa pojedynczego ziarna $\text{Al}(\text{OH})_3$, SEM, 10000×

Plansza II

Fot. 4–7. Agregaty kryształów korundu uzyskanych przy zastosowaniu tlenochloru glinu jako mineralizatora:

- 4 — agregatowe ziarna korundu, SEM, 200×,
- 5 — budowa agregatowa, SEM, 2000×,
- 6 — pokrój poszczególnych ziarn w agregacie, SEM, $\approx 1300\times$,
- 7 — pokrój poszczególnych ziarn w agregacie, SEM, $\approx 13000\times$

Plansza III

Fot. 8–9. Ziarna krystaliczne technicznego tlenku glinu $\alpha\text{-Al}_2\text{O}_3$, SEM:

- 8 — 200×,
- 9 — 20 000×

Plansza IV

Fot. 10–13. Techniczny $\alpha\text{-Al}_2\text{O}_3$ otrzymany przy zastosowaniu tlenochloru glinu jako mineralizatora:

- 10 — mono- i polikryształy $\alpha\text{-Al}_2\text{O}_3$, SEM, 200×,
- 11 — budowa agregatowa $\alpha\text{-Al}_2\text{O}_3$, SEM, 1000×,
- 12 — budowa agregatowa \perp do osi agregatu, SEM, 20 000×,
- 13 — budowa agregatowa $//$ do osi agregatu, SEM, 10 000×

Fot. 14–16. Agregaty kryształów korundu otrzymanych przy zastosowaniu AlF_3 jako mineralizatora:

- 14 — budowa sferyczna agregatów, SEM, 200×,
- 15 — pokrój pojedynczych ziarn krystalicznych w agregacie, SEM, 2000×,
- 16 — pokrój pojedynczych ziarn krystalicznych w agregacie, SEM, 10 000×

Леокадия КУХАРСКА, Анджей ШИМАНЬСКИ

ВЛИЯНИЕ ХЛОРИДНЫХ ИОНОВ НА ВОЗРАСТАНИЕ КРИСТАЛЛОВ КОРУНДА ПРИ КАЛЬЦИНАЦИИ ГИДРАРГИЛЛИТА

Резюме

Важным технологическим параметром окиси алюминия получаемого посредством кальцинации гидраргиллитовой фазы является габитус, размеры и структура кристаллов корунда $\alpha\text{-Al}_2\text{O}_3$. Предыдущими исследованиями констатировано, что минерализующие добавки могут значительно понизить температуру фазовых преобразований $\gamma \rightarrow \delta \rightarrow \theta \rightarrow \alpha\text{-Al}_2\text{O}_3$.

В работе представлены результаты исследований процесса кальцинации гидраргиллита в присутствии хлоридных ионов, которые вводятся в виде $\text{AlOCl} \cdot n\text{H}_2\text{O}$, избранного как наиболее пригодный минерализатор, позволяющий уже при температуре 1523 K получить 98–100% преобразования гидраргиллита в корунд.

Получаемые кристаллы корунда образуются как псевдоморфические агрегаты замещающие зерна гидраргиллита и характеризуются плотной упаковкой кристаллов входящих в состав агрегата. Элементарные составные кристаллы имеют плитчатый габитус и размеры 3 μm . Констатировано правдоподобие диффузионного механизма процесса кальцинации.

ОБЪЯСНЕНИЯ СНИМКОВ

Планшет I

Fot. 1–3. Зерна гидроокиси алюминия полученной в процессе Байера:

- 1 — моно- и поликристаллы $\text{Al}(\text{OH})_3$, SEM, 200×,
- 2 — монокристалл $\text{Al}(\text{OH})_3$ гексагонального габитуса SEM, 1000×,
- 3 — агрегатное строение одиночного зерна $\text{Al}(\text{OH})_3$, SEM, 10 000×

Планшет II

Fot. 4–7. Агрегаты кристаллов корунка полученные при применении $\text{AlOCl} \cdot n\text{H}_2\text{O}$ как минерализатора:

- 4 — агрегатные зерна корунда, SEM, 200×,
- 5 — агрегатное строение, SEM, 2000×,
- 6 — габитус отдельных зерен в агрегате, SEM, $\approx 1300\times$,
- 7 — габитус отдельных зерен в агрегате, SEM, $\approx 13000\times$

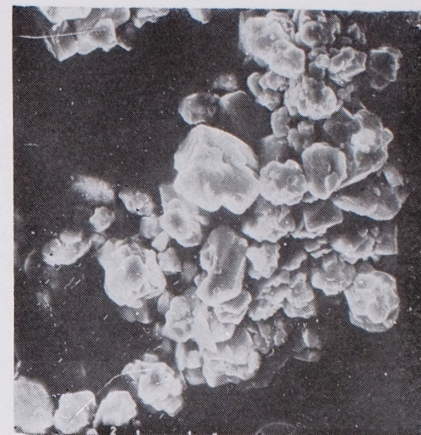
Фот. 8—9. Кристаллические зерна технической окиси: алюминия α - Al_2O_3 , SEM:
8 — $200\times$, 9 — $20\,000\times$

Планшет IV

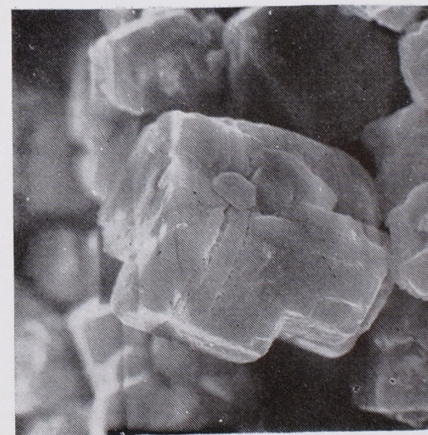
Фот. 10—13. Технический α - Al_2O_3 полученный при применении $\text{AlOCl}\cdot n\text{H}_2\text{O}$ как минерализатора:
10 — моно- и поликристаллы α - Al_2O_3 , SEM $200\times$,
11 — агрегатное строение α - Al_2O_3 , SEM $1000\times$,
12 — агрегатное строение \perp к оси агрегата, SEM, $20\,000\times$,
13 — агрегатное строение \parallel к оси агрегата, SEM, $10\,000\times$

Планшет V

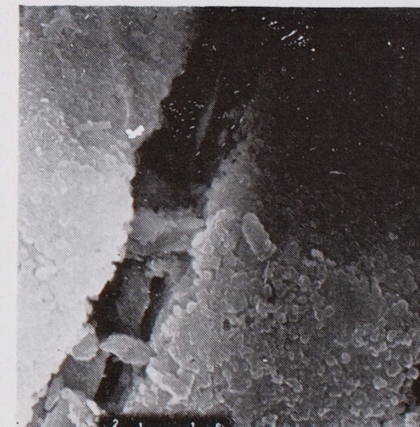
Фот. 14—16. Агрегаты кристаллов корунда полученных при применении AlF_3 как минерализатора
14 — сферическое строение агрегатов, SEM, $200\times$,
15 — габитус отдельных кристаллических зерен в агрегате, SEM, $2000\times$,
16 — габитус отдельных кристаллических зерен в агрегате, SEM, $10\,000\times$



Phot. 1



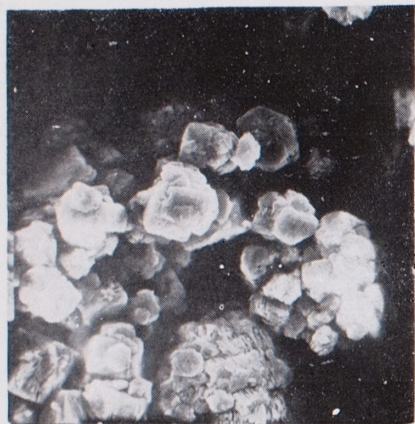
Phot. 2



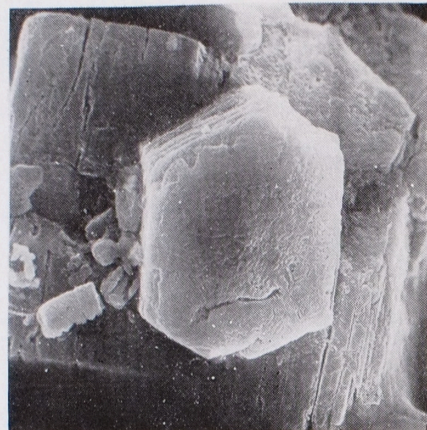
Phot. 3

Phot. 1—3. Aluminium hydroxide grains from Bayer process:
1 — mono- and polycrystals of $\text{Al}(\text{OH})_3$, SEM, $200\times$, 2 — monocrystal of $\text{Al}(\text{OH})_3$ with hexagonal habit, SEM, $1000\times$, 3 — aggregate composition of $\text{Al}(\text{OH})_3$ single grain, SEM, $10\,000\times$

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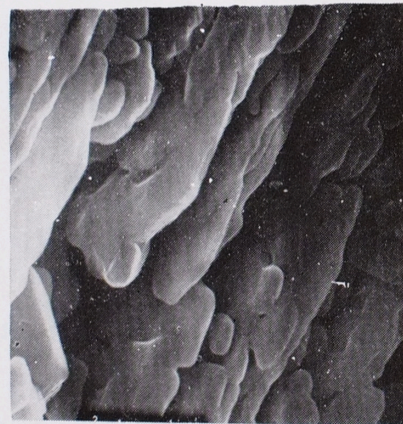
Phot. 4



Phot. 5



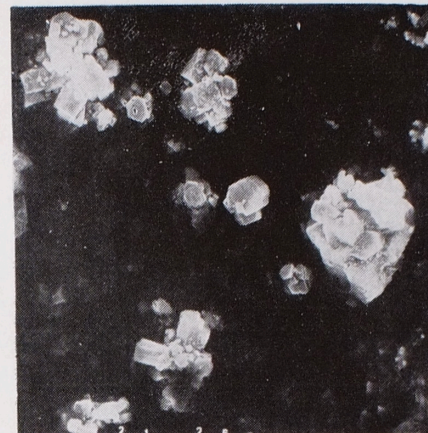
Phot. 6



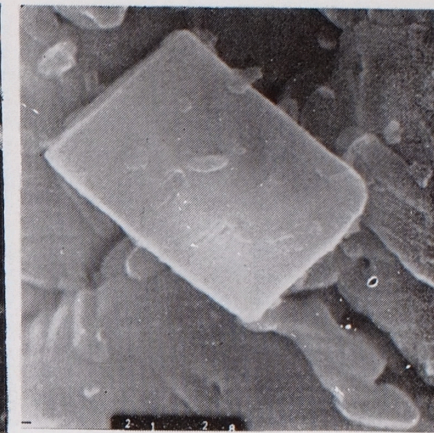
Phot. 7

Phots. 4—7. Aggregates of corundum crystals mineralized with aluminium oxychloride:
 4 — aggregate grains of corundum, SEM, 200×, 5 — aggregate structure, SEM 2000×, 6 — crystal habit of elementary grains in an aggregate, SEM, ≈ 1300×, 7 — crystal habit of elementary grains in an aggregate, SEM, ≈ 13 000×

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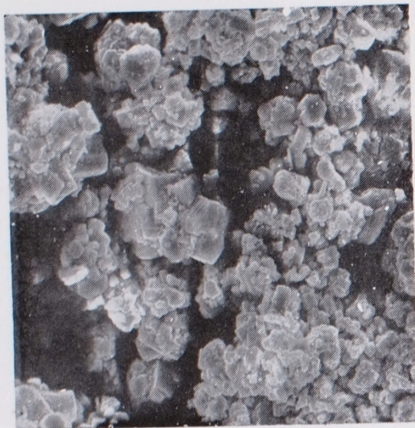
Phot. 8



Phot. 9

Phots. 8—9. Crystal grains of technical alumina α -Al₂O₃, SEM:
 8 — 200×, 9 — 20 000×

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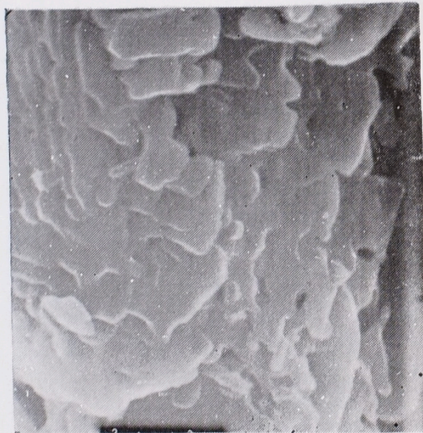
Phot. 10



Phot. 11



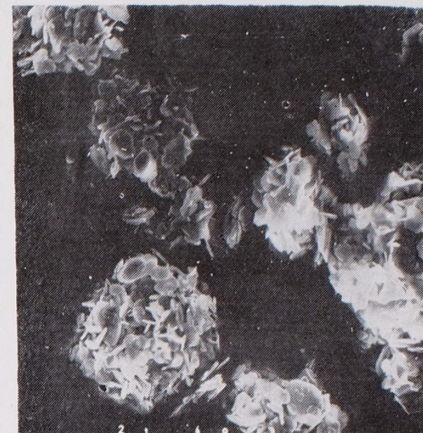
Phot. 12



Phot. 13

Phots. 10—13. Technical alumina $\alpha\text{-Al}_2\text{O}_3$ mineralized with aluminium oxychloride: 10 — mono- and polycrystals of $\alpha\text{-Al}_2\text{O}_3$, SEM, 200 \times , 11 — aggregate structure of $\alpha\text{-Al}_2\text{O}_3$, SEM, 1000 \times , 12 — aggregate structure \perp to aggregate axis, SEM, 20 000 \times , 13 — aggregate structure \parallel to aggregate axis, SEM, 10 000 \times

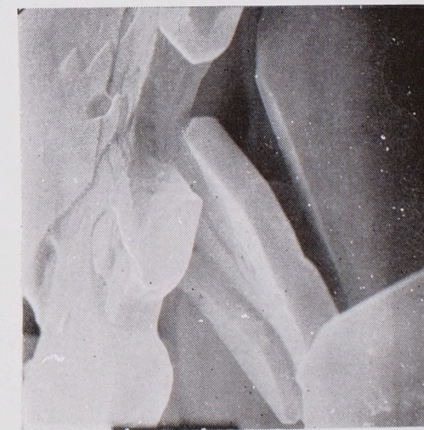
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Phot. 14



Phot. 15



Phot. 16

Phots. 14—16. Aggregates of corundum crystals mineralized with AlF_3 : 14 — spherical structure of aggregates, SEM, 200 \times , 15 — crystal habit of elementary grains in an aggregate, SEM, 2000 \times , 16 — crystal habit of elementary grains in an aggregate, SEM, 10 000 \times

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