

Původní práce

SYNTHESIS OF SOME FERRITES IN MOLTEN SALT MEDIA

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A method was worked out for the preparation of dispersed powdered magnesium, calcium and zinc ferrites by precipitation in the medium of molten salts. The synthesis of compounds in melts, compared to the classical solid phase reaction and the preparation from a suitable precursor, has the advantage of allowing the size, and sometimes also the morphology of the crystals, to be controlled. However, the main advantage of molten salts as a reaction medium is based on its convenient thermodynamic and transport properties. The study was concerned with investigating the effect of temperature and time of heating on the dispersity and morphology of the ferrites in question. It was found that the synthesis can be effected at considerably lower temperatures than the direct synthesis from oxides, and the products show a high phase purity and a comparatively narrow log-normal particle size distribution of crystals with the mean size of less than 1 μm.

INTRODUCTION

Inorganic ionic melts have been recognized as promising media for the synthesis of some compounds, particularly those exhibiting outstanding electrical or magnetic properties, such as ferrites, chromites, titanates, etc. which find application in electronics [1 through 7]. Some ferrites and chromites, and possibly other compounds with a spinel or perovskite structure, are highly topical as inert anode materials for electrochemical production of aluminium [8]. Titanates of various metals doped with a suitable oxide in higher oxidation state are convenient anode materials for molten carbonate fuel cells [9].

The classical preparation of these materials by solid state reactions is characterized by a low rate of the reaction which is controlled by diffusion of the reacting compounds; this results in the use of high temperatures and long times of firing. The technology based on suitable precursors such as hydroxides, alkoxides, carbonates or nitrates [10] saves energy, but does not allow the dispersity of the final product to be controlled.

Precipitation of the compounds from a suitable mixture of molten salts is advantageous not only from the standpoint of kinetics, but also from that of the thermodynamic properties of the reaction medium, namely the values of the Gibbs energy of the reacting substances. Use is made of the differences in the solubility of the reactants and those of the products, as well as of the high thermal and chemical stability of the reaction products. The synthesis in molten salt media has the major advantage in that the particle size, and sometimes even the morphology of the product, can be controlled by suitable selection of reaction time and temperature. Such a control is very significant for subsequent sintering of the powdered product into the final form with the desired porosity.

The main advantage provided by molten salts as the reaction medium for the preparation of mixed oxides is based on a substantial increase in the negative value of the Gibbs energy in the reaction producing the respective compound. Table I

Table I
Gibbs energy of the formation of ferrites

| Phase | ΔG_r^0 kJ mol ⁻¹ | | | Reaction No. |
|-------------|----------------------------------------|---------|---------|--------------|
| | 1 100 K | 1 200 K | 1 300 K | |
| $MgFe_2O_4$ | —203.5 | —210.7 | —216.8 | (2) |
| | —6.7 | —5.7 | —4.8 | (1) |
| $CaFe_2O_4$ | —98.6 | —111.7 | —124.2 | (2) |
| | —31.4 | —32.4 | —33.4 | (1) |
| $ZnFe_2O_4$ | —164.1 | —184.2 | —198.9 | (2) |
| | —21.7 | —12.9 | —4.1 | (1) |

lists the values of Gibbs energies for the individual reactions forming the ferrites by direct synthesis from the respective oxides and by precipitation in molten salt media. In the first case, the Gibbs energy values correspond to the reaction



and in the other to the reaction using chlorides,



The values required for the calculation of Gibbs energy values were taken over from ref. [11].

The first stage of research into the synthesis of mixed oxides in molten salt media was aimed at working out a method for their preparation and identification. The effect of temperature and time of heating on the dispersity and morphology of $MgFe_2O_4$, $CaFe_2O_4$ and $ZnFe_2O_4$ was studied.

EXPERIMENTAL

The following reagents were used in the synthesis of the ferrites: Fe_2O_3 , A. R. grade, USSR, $MgCO_3$, A. R. grade, Neratovice, $CaCO_3$, A. R. grade, Lachema, $CaCl_2 \cdot 2 H_2O$, C. P. grade, Lachema, $ZnCO_3$, C. P. grade, Lachema, $ZnCl_2$, A. R. grade, anhydrous, Merck, $NaCl$, A. R. grade, Lachema, KCl , A. R. grade, Lachema, and Na_2CO_3 , A. R. grade, Lachema. The dehydration was effected by vacuum drying at 200 °C in the presence of P_2O_5 .

The initial mixtures of salts were weighed in a platinum crucible and fused in a muffle kiln heated at the chosen temperature. The total amount of the mixture was about 15 to 20 g. Use was made of a three-fold excess of sodium chloride (at 900 °C), potassium chloride (at 800 °C) or an equimolar $NaCl$ — KCl mixture (at 700 °C). After cooling, the mixture was dissolved in hot water, the undissolved residue rinsed several times with distilled water and filtered off on a Büchner

funnel. The filter cake was dried at 120 °C. The compounds thus prepared were identified by X-ray diffraction analysis.

The morphology and particle size distribution of the powdered products were determined by means of the scanning electron microscope. The percent occurrence of crystals in the individual size classes was determined on SEM micrographs by measuring the mean size of the separate grains as the arithmetic mean of the

Table II

Logarithmic-normal size distribution parameters of MgFe_2O_4 crystals

| t °C | τ h | \bar{d} μm | $\ln \bar{d}_i$ | $\sigma (\ln d)$ | N |
|-----------|-------------|-----------------|-----------------|------------------|-----|
| 700 | 2 | 0.241 | -1.446 | 0.279 | 120 |
| 800 | 2 | 0.319 | -1.187 | 0.449 | 120 |
| 900 | 2 | 0.409 | -0.486 | 0.415 | 100 |
| 1000 | 2 | 0.512 | -0.658 | 0.294 | 85 |
| 900 | 1 | 0.326 | -1.199 | 0.320 | 90 |
| 900 | 3 | 0.549 | -0.630 | 0.306 | 110 |
| 900 | 4 | 0.678 | -0.433 | 0.283 | 85 |

Table III

Logarithmic-normal size distribution parameters of CaFe_2O_4 crystals

| t °C | τ h | \bar{d} μm | $\ln \bar{d}_i$ | $\sigma (\ln d)$ | N |
|-----------|-------------|-----------------|-----------------|------------------|-----|
| 800 | 2 | 0.946 | -0.098 | 0.422 | 110 |
| 900 | 2 | 1.089 | -0.023 | 0.492 | 70 |
| 1000 | 2 | 1.190 | -0.061 | 0.484 | 65 |
| 900 | 0.5 | 0.384 | -0.894 | 0.395 | 95 |
| 900 | 1.5 | 0.768 | -0.652 | 0.357 | 75 |
| 900 | 3 | 1.350 | 0.074 | 0.283 | 60 |
| 900 | 3 | 1.280 | 0.051 | 0.326 | 55 |

Table IV

Logarithmic-normal size distribution parameters of ZnFe_2O_4 crystals

| t °C | τ h | \bar{d} μm | $\ln \bar{d}_i$ | $\sigma (\ln d)$ | N |
|-----------|-------------|-----------------|-----------------|------------------|-----|
| 700 | 2 | 0.438 | -0.084 | 0.234 | 95 |
| 800 | 2 | 0.475 | -0.942 | 0.499 | 125 |
| 900 | 2 | 0.519 | -0.624 | 0.289 | 90 |
| 1000 | 2 | 0.569 | -0.279 | 0.378 | 80 |
| 900 | 1 | 0.382 | -1.107 | 0.405 | 120 |
| 900 | 3 | 0.888 | -0.155 | 0.334 | 100 |
| 900 | 4 | 1.162 | 0.213 | 0.413 | 75 |

largest and the smallest dimension. The relative representation of crystals in the size classes was described by means of log-normal distribution and the mean crystal size in the sample was determined. On the basis of this evaluation, the dependence of mean crystal size on the temperature and time of heating was established. The respective values of mean crystal size, standard deviation of the logarithm of crystal size (diameter) and total occurrence of the whole set are listed in Tables II through IV for the temperatures and times of heating studied.

RESULTS AND DISCUSSION

The magnesium ferrite, $MgFe_2O_4$, was prepared by reacting ferric oxide with magnesium carbonate in the medium of molten sodium chloride, potassium chloride or their mixture. The possibility of using anhydrous magnesium chloride with sodium carbonate was also verified. In both cases the reaction yielded magnesium ferrite, $MgFe_2O_4$, and the alternative utilization of magnesium chloride or carbonate had no effect on the morphology of the final product. The effect of temperature and time of heating on the size of crystals was studied over the temperature range of 700 to 1000 °C and times of heating from 1 to 4 hours. Fig. 1 shows the

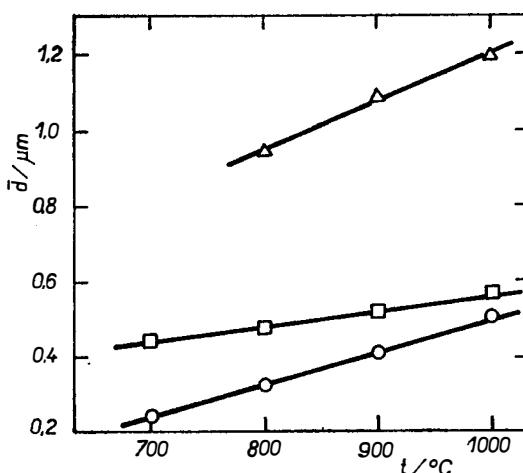


Fig. 1. Mean crystal size vs. temperature at a constant heating time of 2 hours;
○ — $MgFe_2O_4$, △ — $CaFe_2O_4$, □ — $ZnFe_2O_4$.

plot of mean magnesium ferrite particle size vs. temperature at a constant time of heating of 2 hours. There is an apparent increase in mean crystal size with rising temperature, which can be attributed to more favourable mass transport properties of the melt at higher temperature. Fig. 2 is a plot of the mean magnesium ferrite particle size vs. heating time at a constant temperature of 900 °C. There is again an increase in the value of mean crystal size resulting from isothermal growth in the presence of the liquid phase. The change in the mean crystal size is obviously linear, which supports the assumption of a reaction-controlled mechanism of crystal growth, i.e. a mechanism involving dissolution and precipitation of the crystallizing phase [12]. For comparison, Figs. 3 and 4 show micrographs of magnesium ferrite

prepared at 700 °C during 2 hours (Fig. 3) and at 900 °C during 3 hours (Fig. 4). Magnesium ferrite belongs to the group of spinels, crystallizing in the cubic system with space group Fd3m, and this was also the morphology of the crystals obtained.

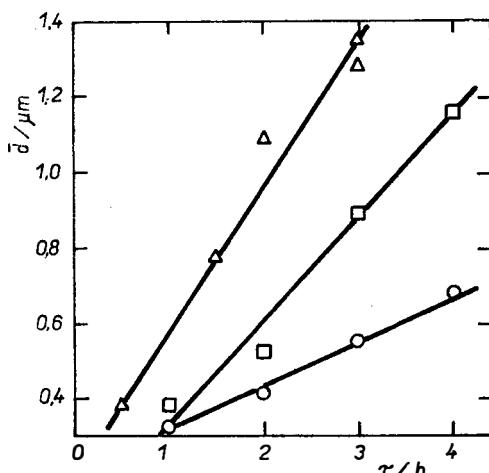


Fig. 2. Mean crystal size vs. time of heating at a constant temperature of 900 °C;
 ○ — MgFe_2O_4 , △ — CaFe_2O_4 , □ — ZnFe_2O_4 .

The calcium ferrite, CaFe_2O_4 , was prepared by reacting ferric oxide with calcium carbonate or anhydrous calcium chloride and sodium carbonate, in the medium of molten sodium chloride, potassium chloride or their mixture. In the case of preparation at 700 °C in the NaCl—KCl mixture the sample was inadequately fused and remained syrupy, so that it had to be discarded from the experimental set. However, replacement of the flux with a NaCl—LiCl mixture (1 : 1 by wt.) resulted in the formation of lithium ferrites LiFeO_2 and LiFe_5O_8 as proved by X-ray powder diffraction and by the change in the morphology of the product as revealed by SEM micrographs. In view of the size of the calcium atom, CaFe_2O_4 does not belong to the spinels, crystallizing in the orthorhombic system with the Pnma spatial group. The effect of temperature over the range of 800 to 1000 °C and the heating time from 0.5 to 3 hours was followed during the preparation of calcium ferrite. The development of crystal morphology can be seen in Figs. 5 and 6, showing micrographs of calcium ferrite prepared at 900 °C during 0.5 hour (Fig. 5) and at 1000 °C during 2 hours (Fig. 6). The plate-shaped crystals first grow preferentially in the direction of one crystallographic axis, acquiring an acicular form. Fig. 1 shows the temperature dependence of mean crystal size of calcium ferrite at constant heating time of 2 hours, Fig. 2 the relation between mean crystal size and the time of heating at a constant temperature of 900 °C. The favourable effect of temperature, improving the transport properties of the melt, and the isothermal growth of crystals in the presence of the liquid phase, is again obvious. The characteristic morphology of calcium ferrite crystals resulted in a faster growth of the mean crystal size with increasing temperature and time of heating as a consequence of the preferential growth in the direction of one crystallographic axis. The composition of the initial mixture was also found to

affect the morphology of the crystals obtained. With calcium chloride, the crystals grow preferentially in the direction of axis *c* whereas with CaCO_3 the growth in this direction is not so marked.

The zinc ferrite was produced by reaction of ferric oxide with zinc carbonate or anhydrous zinc chloride and sodium carbonate in the medium of molten sodium chloride, potassium chloride or the $\text{NaCl}-\text{KCl}$ mixture at 1 : 1 ratio. The effect of temperature and heating time on the size of crystals was investigated over the temperature range of 700 to 1 000 °C and the heating time of 1 to 4 hours. The dependence of mean crystal size on temperature at a constant heating time is plotted in Fig. 1, and that on the heating time at a constant heating temperature of 900 °C in Fig. 2. Among all the three ferrites studied, zinc ferrite showed the least effect of temperature on crystallization rate. The influence of the heating time is much greater. Fig. 7 shows a micrograph of zinc ferrite obtained at 700 °C during 2 hours, and Fig. 8 of zinc ferrite produced at 900 °C also during 2 hours. The morphology of the crystals obtained corresponds to the spinel structure of zinc ferrite; there was no difference between the use of zinc carbonate and zinc chloride.

As follows from Tables II through IV, the particle sizes of the ferrite crystals prepared all show log-normal distribution with a standard deviation of the logarithm of crystal diameter in the range of 0.23 to 0.5, which indicates a relative narrow size distribution of the crystals. X-ray diffraction analysis showed that in some cases the final products were contaminated with unreacted reactants (ZnO , $\text{Ca}(\text{OH})_2$, etc.). Even though this contamination was at a low level, the final powdered product will have to be washed with dilute acid. This procedure was not employed in the present study in order to assess the quantitative course of the synthesis.

It may be concluded that the preparation of mixed oxides by precipitation in molten salt media appears to be a very promising method for the following reasons:

(i) the reaction can be effected at substantially lower temperatures than the direct synthesis from oxides,

(ii) in view of the favourable mass transport properties of molten salts it is possible to influence the particle size, the size distribution and possibly also the morphology of the grains of the respective powders,

(iii) the powdered products can be prepared with a high degree of purity as the undesirable admixtures or reaction products are readily soluble or gaseous,

(iv) in all the instances, the particle size distribution of the powders obtained is described by a comparatively narrow log-normal distribution. In most cases, the mean crystal size was less than 1 μm , which is very favourable with respect to further processing of the powders.

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SYNTÉZA NIEKTORÝCH FERITOV V PROSTREDÍ ROZTAVENÝCH SOLÍ

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Rozpracovala sa metóda prípravy disperzných práškov feritu horečnatého, vápenatého a zinočnatého precipitáciou v prostredí roztavených solí. Prednosťou syntézy zlúčenín v taveninách oproti klasickej príprave reakciou v tuhej fáze a príprave pomocou vhodného prekurzora je najmä možnosť regulácie veľkosti a niekedy aj morfológie kryštálov. Hlavná výhoda použitia roztavených solí ako reakčného média spočívá vo výhodných termodynamických a transportných vlastnostiach reakčného prostredia. V práci sa skúmal vplyv teploty a doby záhrevu na disperzitu a morfológiu sledovaných feritov. Zistilo sa, že syntézu možno uskutočniť pri podstatne nižších teplotách ako priamu syntézu z oxidov, pričom produkty sa vyznačujú vysokou fázovou čistotou a ponierne úzkym log-normálnym rozdelením veľkosti kryštálov so strednou veľkosťou niemšou ako 1 μm .

Obr. 1. Závislosť strednej veľkosti kryštálov od teploty pri konštantnom čase záhrevu 2 h;
○ — MgFe₂O₄, △ — CaFe₂O₄, □ — ZnFe₂O₄.

Obr. 2. Závislosť strednej veľkosti kryštálov od doby záhrevu pri konštantnej teplote 900 °C;
○ — MgFe₂O₄, △ — CaFe₂O₄, □ — ZnFe₂O₄.

Obr. 3. SEM mikrosnímkova prášku MgFe₂O₄ pripraveného pri teplote 700 °C počas 2 h.

Obr. 4. SEM mikrosnímkova prášku MgFe₂O₄ pripraveného pri teplote 900 °C počas 3 h.

Obr. 5. SEM mikrosnímkova prášku CaFe₂O₄ pripraveného pri teplote 900 °C počas 0,5 h.

Obr. 6. SEM mikrosnímkova prášku CaFe₂O₄ pripraveného pri teplote 1000 °C počas 2 h.

Obr. 7. SEM mikrosnímkova prášku ZnFe₂O₄ pripraveného pri teplote 700 °C počas 2 h.

Obr. 8. SEM mikrosnímkova prášku ZnFe₂O₄ pripraveného pri teplote 900 °C počas 2 h.

СИНТЕЗ НЕКОТОРЫХ ФЕРРИТОВ В СРЕДЕ РАСПЛАВЛЕННЫХ СОЛЕЙ

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Был разработан метод получения дисперсных порошков феррита магния, кальция и цинка пропицацией в среде расплавленных солей. Преимущество синтеза соединений в расплавах по сравнению с классическим получением путем реакции в твердой фазе и по сравнению с получением с помощью пригодного прекурсора заключается прежде всего в возможности регулировать размер и иногда и морфологию кристаллов. Основное преимущество применения расплавленных солей в качестве реакционной среды имеется в пригодных термодинамических и транспортных свойствах реакционной среды. В предлагаемой работе рассматривается влияние температуры и времени нагрева на дисперсионную способность и морфологию исследуемых ферритов. Было установлено, что синтез можно проводить при существенно более низких температурах чем у прямого синтеза из оксидов, причем продукты обозначены высокой фазовой чистотой и относительно узким лог-нормальным распределением размера кристаллов со средним размером ниже 1 μm .

- Рис. 1. Зависимость среднего размера кристаллов от температуры при постоянном времени нагрева 2 ч.; о — MgFe₂O₄; △ — CaFe₂O₄, □ — ZnFe₂O₄.
- Рис. 2. Зависимость среднего размера кристаллов от времени нагрева при постоянной температуре 900 °C: о — MgFe₂O₄; △ — CaFe₂O₄, □ — ZnFe₂O₄.
- Рис. 3. SEM микрография порошка MgFe₂O₄, полученного при температуре 700 °C и времени 2 ч.
- Рис. 4. SEM микрография порошка MgFe₂O₄, полученного при температуре 900 °C и времени 3 ч.
- Рис. 5. SEM микрография порошка CaFe₂O₄, полученного при температуре 900 °C и времени 0,5 ч.
- Рис. 6. SEM микрография порошка CaFe₂O₄, полученного при температуре 1000 °C и времени 2 ч.
- Рис. 7. SEM микрография порошка ZnFe₂O₄, полученного при температуре 700 °C и времени 2 ч.
- Рис. 8. SEM микрография порошка ZnFe₂O₄, полученного при температуре 900 °C и времени 2 ч.

MODERN CRYSTALLOGRAPHY IV₁— PHYSICAL PROPERTIES OF CRYSTALS (Moderná kryštalografia IV — fyzikálne vlastnosti kryštálov; preklad z ruského originálu „Sovremennaja kristallografiya“. Editor L. A. Šuvalov. Springer-Verlag Berlin Heidelberg New York London Paris Tokyo 1988. 583 str., 270 obr., 65 tab., cena 198 DM.

Štvrtý diel kompendia „Sovremennaja kristallografiya“ je venovaný kryštalofyzike, recenzie predošlých troch dielov pozri Silikaty 26, 354 (1982); 27, 106 (1983); 29 191 (1985). Obsah je rozdelený do ôsmich kapitol:

1. L. A. Šuvalov: Základy tenzorového a symetrického opisu fyzikálnych vlastností kryštálovo (tenzorový aparát kryštalofyziky a všeobecné problémy symetrie fyzikálnych vlastností kryštálov) 49 strán, 16 odkazov.

2. A. A. Urusovskaja: Mechanické vlastnosti kryštálov (elastické vlastnosti, plastické skl佐é deformácie, pohyb dislokácií, difúzne mechanizmy, mechanické dvojčatenie, lom, a príslušné, experimentálne metódy). 128 strán, 104 odkazov.

3. I. S. Želudev: Elektrické vlastnosti kryštálov (polarizácia, vodivosť, dielektrické straty, piezo-, pyroelektrické javy a elektrostriktia, doménové štruktúry a elektrické vlastnosti feroelektrík a antielektrík spolu s vybranými príkladmi konkrétnych štruktúr, fázové transformácie feroelektrík) 89 strán, 23 odkazov.

4. A. V. Zalesskij: Magnetické vlastnosti kryštálov (neuspriadané a uspriadané magnetiká, doménové štruktúry feromagnetík a magnetizačný proces, anizotropia feromagnetík, štruktúry niektorých magneticky uspriadaných kryštálov, piezo- a magnetoelektrické javy). 81 strán, 17 odkazov.

5. S. A. Semiletov: Polovodivé kryštály (základné vlastnosti polovodičov, p-n prechody). 28 strán, 12 odkazov.

6. S. A. Semiletov: Transportné javy v kryštáloch (elektrická a tepelná vodivosť, termoelektrické efekty, galvanovo a termomagnetické efekty). 29 strán, 9 odkazov.

7. B. N. Grečušnikov: Optické vlastnosti kryštálov (šírenie elektromagnetických vln v anizotropnom prostredí, jedno- a dvojsové kryštály, dvojlam, interferenčné javy, absorpcia, optická aktívita, elektro-, magneto- a piezooptické vlastnosti, disperzia, nelineárna optika, základy teórie kryštálového poľa, lasery, polarizovaná luminiscencia, elektrónová paramagnetická rezonancia iónov nečistôt). 108 strán, 85 odkazov.

8. I. G. Čistjakov, S. A. Píkin: Kvapalné kryštály (základné charakteristiky, textúra a optické vlastnosti, teória kvapalnokryštálického stavu, magnetické, elektrické a teplotné vlastnosti). 57 strán, 18 odkazov.

Jednotlivé kapitoly sú napísané prístupným spôsobom, vhodne na seba nadvážujú a text sa dobre číta. Obzvlášť potešiteľná je dokonalá znalosť modernej krytalografie a dôsledné používanie jej pojmov a aparátu. L. A. Šuvalov si zaslúži uznanie za vzorý editorský výkon. Kniha je výbornou príručkou pre vedeckých i výskumných pracovníkov ako aj pre vysokoškolských učiteľov a nemala by chýbať v knižnici žiadneho ústavu s krytalografickým a materiálovedným zameraním.

Ďurovič

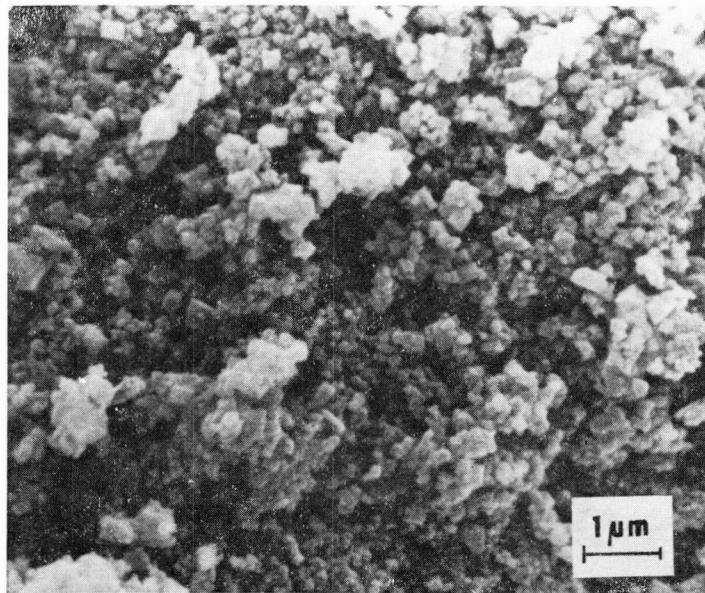


Fig. 3. SEM micrograph of MgFe₂O₄ powder prepared at 700 °C for 2 hrs;

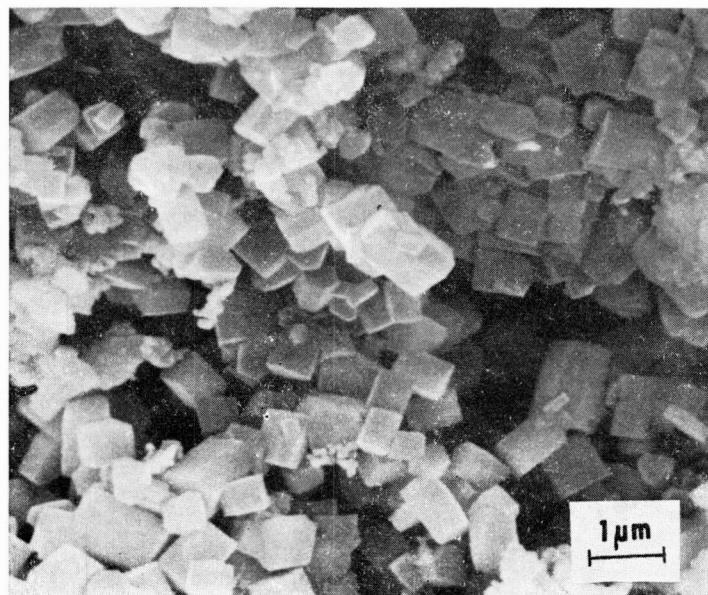


Fig. 4. SEM micrograph of MgFe₂O₄ powder prepared at 900 °C for 3 hrs.

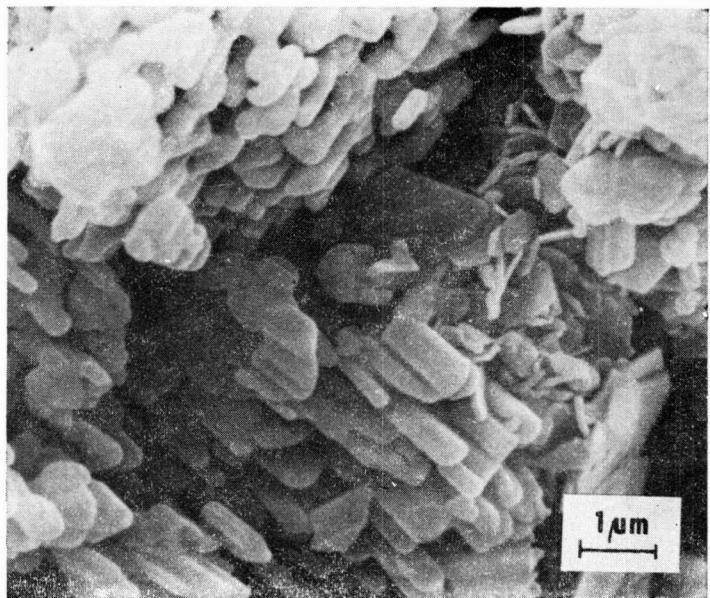


Fig. 5. SEM micrograph of CaFe_2O_4 powder prepared at 900°C for 0.5 hrs.

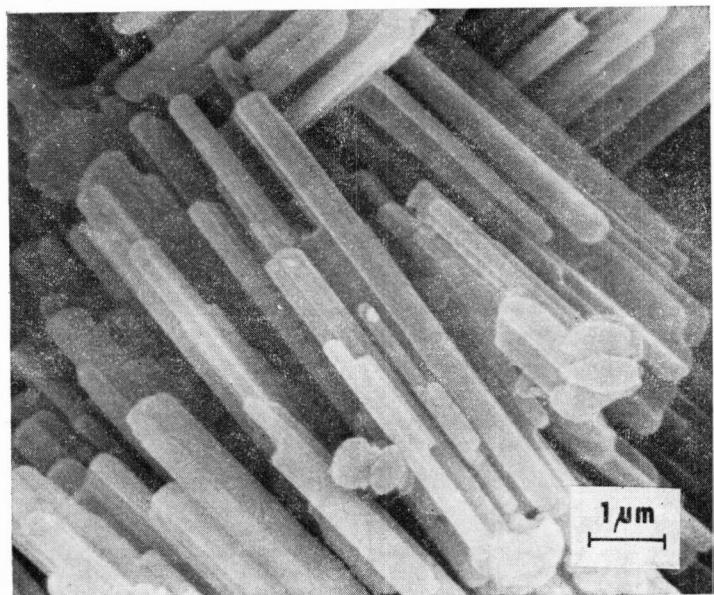


Fig. 6. SEM micrograph of CaFe_2O_4 powder prepared at 1000°C for 2 hrs.

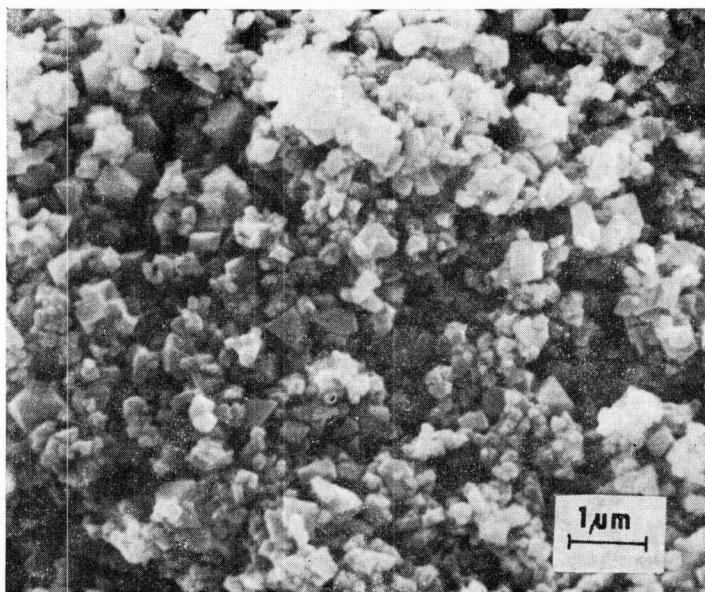


Fig. 7. SEM micrograph of ZnFe₂O₄ powder prepared at 700 °C for 2 hrs.

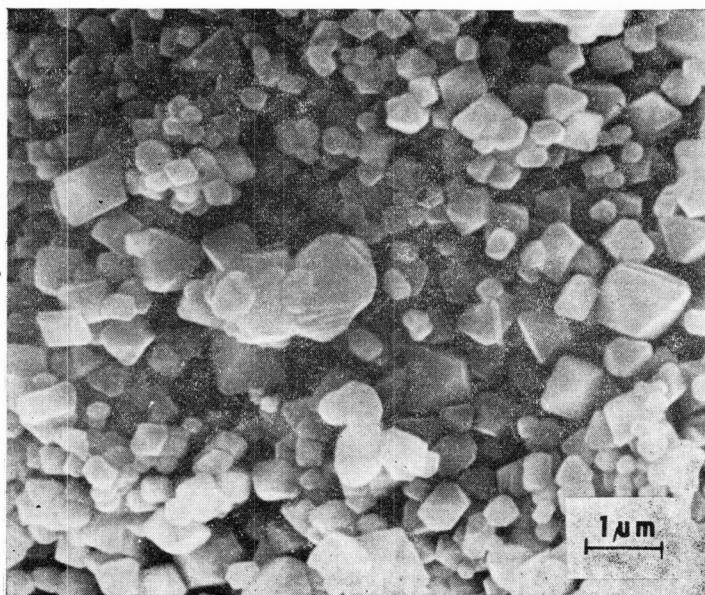


Fig. 8. SEM micrograph of ZnFe₂O₄ powder prepared at 900 °C for 2 hrs.