

SYNTHESIS OF SOME TITANATES IN MOLTEN SALTS

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Finely dispersed powders of lithium, calcium and strontium titanates were prepared by precipitation in molten salts. The influence of temperature and of the time of heat treatment on the mean crystal size was determined. The mean crystal size was found to increase with temperature and time, however, at a constant temperature the rate of crystal growth slowed down with time. This indicated that the isothermal crystal growth is not an isolated process and is apparently accompanied by formation of new crystallization nuclei. It is assumed that the crystallization process is governed by two different mechanisms: in the initial stage, the crystal growth is controlled by surface reaction while in the subsequent stage, with the formation of a concentration gradient at the phase boundary, diffusion becomes the predominant factor and the rate of the crystallization is gradually slows down.

INTRODUCTION

Inorganic ionic melts, i.e. mixtures of chlorides or sulphates of bivalent metals with alkali chlorides or sulphates, have recently been successfully employed as reaction media in chemical synthesis of mixed oxide powders [1—8]. Ferrites, chromites, titanates and some other mixed oxides exhibit specific electrical and magnetic properties which make them interesting for microelectronics and other applications. For example, titanates of various metals doped with a suitable oxide in a higher oxidation state are considered to be promising anode materials for molten carbonate fuel cells [9].

The conventional preparation of mixed oxides by solid state reactions requires high temperatures and long reaction times. It is also characterized by a low reaction rate which is controlled by diffusion of the reactants. The synthesis of powders from suitable precursors consisting of hydroxides, alkoxides, carbonates or nitrates, although energetically not so demanding, often leads to formation of porous grains or agglomerates in the final product.

The use of molten salts as reaction media for the preparation of mixed oxides appears to be advantageous for several reasons: It makes it possible to control the size and, to a certain extent, also the morphology of the particles by selecting a suitable temperature and reaction time (duration of the heat treatment). Besides, as evidenced by Table I, Gibbs reaction energies of the formation of titanates by precipitation from molten salts mostly exhibit more negative values compared with the direct synthesis from the respective oxides. The values presented in Table I correspond to direct synthesis from oxides,



to precipitation from chlorides,



and from sulphates

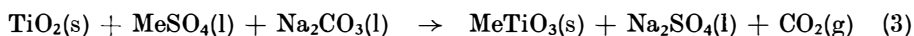


Table I

Values of Gibbs reaction energy of the formation of titanates (1200 K)

Titanate	$\frac{\Delta G_r^0}{\text{kJ mol}^{-1}}$	Reaction
Li ₂ TiO ₃	-131.6	1
	-135.5	2
	-103.9	3
CaTiO ₃	-87.0	1
	-167.0	2
	-132.6	3
SrTiO ₃	-135.5	1
	-171.1	2
	-145.2	3

LiCl as well as Li₂SO₄ were used in the synthesis of Li₂TiO₃). Gibbs energy values tabulated by Barin and Knacke [10] were employed in the calculations.

In the present work, the influence of the reaction temperature and time on the dispersity and morphology of the synthesized Li₂TiO₃, CaTiO₃ and SrTiO₃ was determined.

EXPERIMENTAL

The following chemicals were employed in the synthesis of the above titanates: TiO₂, NaCl, LiCl and KCl "reagent grade" (LACHEMA), Li₂SO₄, CaSO₄ · 2 H₂O, H₂SO₄ and Na₂CO₃, A.R. (LACHEMA) and SrCO₃ "For Electroceramics" (LACHEMA). Strontium sulphate was prepared from an aqueous suspension of strontium carbonate by reaction with sulphuric acid. The chemicals employed were vacuum dried over P₂O₅ at 200 °C.

The reaction mixtures were melted in a platinum crucible in a muffle furnace. The total weighed-in amount was 20 g.

Different fluxes have been employed depending on the reaction temperature: sodium chloride (at 900 °C), potassium chloride (at 800 °C) and KCl — Na₂CO₃ mixture 1 : 1 by wt. (at 700 °C). After cooling, the reaction mixture was dissolved in hot water. The insoluble residue (the reaction product) was washed with distilled water, filtered in a Büchner funnel and dried at 120 °C.

The reaction products were identified by X-ray powder diffraction. The characteristic lines of lithium, calcium and strontium titanates only were identified on the respective diffraction patterns which indicated a high purity of the mixed oxides synthesized. The morphology and dispersity of the produced powders was determined by means of the JEOL X5C scanning electron microscope. The size of the individual crystals considered in the evaluation of the mean crystal size corresponds to the arithmetical mean of the maximum and minimum dimensions determined on the microphotographs. The distribution of the particles of the synthesized powders was described by logarithmic-normal distribution.

The mean crystal sizes of titanates synthesized at different temperatures and reaction times are listed in Table II. Based on the evaluation of the experimental

results, the influence of the reaction temperature and reaction time on the growth of the mean crystal size, and the dependence of the standard deviation of the particles diameter on the reaction time at 900 °C were determined.

Table II

Values of mean size of Li_2TiO_3 , CaTiO_3 and SrTiO_3 crystals prepared at different conditions

$t/^\circ\text{C}$	τ/h	$\bar{d}/\mu\text{m}$		
		Li_2TiO_3	CaTiO_3	SrTiO_3
700	4	0.446	0.044	0.162
800	4	0.662	0.074	0.216
900	1	0.928	0.104	0.189
900	2	1.251	0.122	0.256
900	3	1.270	0.120	0.281
900	4	1.352	0.146	0.343

RESULTS AND DISCUSSION

Lithium titanate, Li_2TiO_3 , was prepared by the reaction of titanium oxide, lithium sulphate and sodium carbonate alternatively in molten NaCl at 900 °C, KCl at 800 °C and in the $\text{KCl} - \text{Na}_2\text{CO}_3$ mixture at 700 °C. The effect of temperature and reaction time (from 1 to 4 h) on the crystal size of synthesized Li_2TiO_3 was determined. As evidenced by the data presented in Table II, the mean crystal size increases with temperature, which may apparently be attributed to the improved transport properties of the melt at higher temperatures. At a constant temperature, the mean crystal size increases with the time of heat treatment, apparently owing to isothermal growth in the presence of a liquid phase.

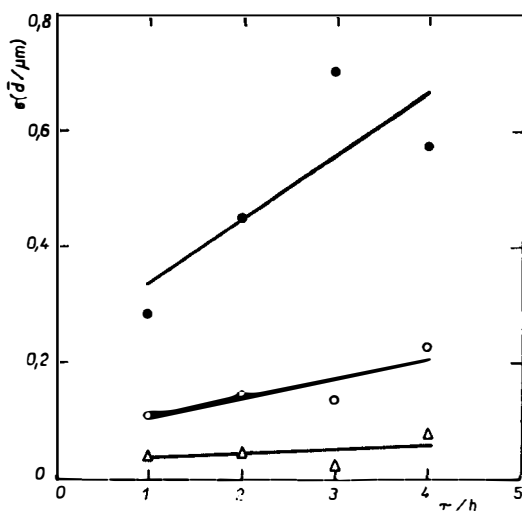


Fig. 1. Standard deviation of the mean particle diameter vs. the time of heat treatment at 900 °C; ● - Li_2TiO_3 ; △ - CaTiO_3 ; ○ - SrTiO_3 .

Fig. 1 shows the standard deviation of the diameter of Li_2TiO_3 particles vs. the time of heating at 900°C . The particle size distribution, characterized by the standard deviation of the particle diameter, increases with the reaction time. On the other hand, the rate of growth of the mean crystal size decreases with time. Consequently, it can be assumed that the isothermal crystal growth is accompanied by secondary formation of crystallization nuclei. Thus it can be assumed that in the initial stage, the mechanism of crystal growth in the multiphase system is controlled by a surface reaction. Subsequently, after the formation of a concentration gradient, the diffusion becomes the predominant factor and the rate of crystal growth slows down. Fig. 2 shows a micrograph of monoclinic lithium titanate synthesized at 900°C for 4 h.

Calcium titanate, CaTiO_3 , was prepared by reacting titanium dioxide with calcium sulphate and sodium carbonate in the respective fluxes. Here again, the dependence of crystal size on temperature (from 700 to 900°C) and the heating time (from 1 to 4 h) was determined. The morphology of the CaTiO_3 crystals can be observed in Fig. 3 showing the micrograph of calcium titanate synthesized at 900°C for 4 h. Calcium titanate belongs to the perovskite group and crystallizes in the tetragonal system. As indicated by the data in Table II, the favourable effect of increasing temperature on the transport properties of the melt and, consequently on the rate of the crystal growth, was also observed.

Fig. 1 shows a plot of the standard deviation of CaTiO_3 particles diameter vs. the reaction time at 900°C . The course of this dependence can be interpreted in the same way as for Li_2TiO_3 .

Strontium titanate, SrTiO_3 , was synthesized by reacting titanium oxide with strontium sulphate and sodium carbonate at 700 , 800 and 900°C in the corresponding fluxes. The time of heat treatment was again varied from 1 to 4 h. The dependence of the standard deviation of the diameter of SrTiO_3 particles on the reaction time, shown in Fig. 1, indicates that also in this case the crystallization is accompanied by formation of secondary crystallization nuclei and the controlling mechanism changes in the course of isothermal crystal growth. Here again an increase in the mean crystal size with increasing temperature reflecting improved transport properties of the melt was observed; however, the influence of the heating time on the rate of the crystal growth was less distinct than in the case of Li_2TiO_3 and CaTiO_3 (see Table II). Fig. 4 shows a micrograph of strontium titanate synthesized at 900°C for 3 h.

As illustrated in Figs. 3 and 4, the mean crystal size of CaTiO_3 and SrTiO_3 is below $1\ \mu\text{m}$ and the isothermal crystal growth is accompanied by the sintering and aggregation of crystals.

CONCLUSION

It can be concluded that the preparation of titanate powders by precipitation in molten salts appears to be advantageous from several aspects:

(i) the synthesis in molten salts can be carried out at substantially lower temperatures compared with direct synthesis from the corresponding oxides;

(ii) owing to the advantageous transport properties of molten salts, the mean grain size of the synthesized powders can largely be controlled by the choice of suitable reaction conditions;

(iii) high-purity titanates can be produced as the by-products of the synthesis are readily soluble in water.

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SYNTEZA NIEKTORÝCH TITANIČITANOV
V PROSTREDÍ ROZTAVENÝCH SOLÍ

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Jemne disperzné prášky titaničitanu lítneho, vápenatého a stronnatého sa pripravili precipitáciou v prostredí roztavených solí. Sledoval sa vplyv teploty a doby záhrevu na strednú veľkosť kryštálov. Zistilo sa, že stredná veľkosť kryštálov vplyvom teploty a času rastie. Nakoľko rýchlosť vzrastu strednej veľkosti kryštálov s časom klesá, možno predpokladať, že v priebehu izotermického rastu kryštálov môže dochádzať k sekundárnej nukleácii kryštálov, čiže proces nukleácie nie je dostatočne separovaný od procesu rastu kryštálov. V priebehu izotermického rastu kryštálov dochádza pravdepodobne k zmene riadiaceho mechanizmu. V počiatočnom štádiu je mechanizmus rastu riadený povrchovou reakciou. V neskoršom štádiu, kedy sa na fázovom rozhraní vytvára koncentračný gradient, prevláda difúziou riadený rast kryštálov a rýchlosť rastu kryštálov klesá.

Obr. 1. Závislosť smerodajnej odchýlky priemeru mikročastic od doby záhrevu pri konštantnej teplote 900 °C; ● - Li_2TiO_3 ; △ - CaTiO_3 ; ○ - SrTiO_3 .

Obr. 2. SEM mikrosnímka práškoveho Li_2TiO_3 pripraveného pri teplote 900 °C počas 4 hodín.

Obr. 3. SEM mikrosnímka práškoveho CaTiO_3 pripraveného pri teplote 900 °C počas 4 hodín.

Obr. 4. SEM mikrosnímka práškoveho SrTiO_3 pripraveného pri teplote 900 °C počas 3 hodín.

СИНТЕЗ НЕКОТОРЫХ ТИТАНАТОВ
В СРЕДЕ РАСПЛАВЛЕННЫХ СОЛЕЙ

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Тонко дисперсные порошки титаната лития, кальция и стронция приготовили преципитацией в среде расплавленных солей. Исследовали влияние температуры и времени нагрева на средний размер кристаллов. Было установлено, что средний размер кристаллов под влиянием температуры и времени растет. До какой степени скорость роста среднего размера с временем понижается, можно вывести из того, что в течение изотермического роста кристаллов может происходить вторичное образование зародышей кристаллов, то есть что процесс образования зародышей не является достаточно отделенным от процесса роста кристаллов. Во время изотермического роста кристаллов правдоподобно происходит изменение управляющего механизма. В начальной стадии

механизм роста управляется поверхностной реакцией. В дальнейшей стадии, когда на разделе фаз создается градиент концентрации, преобладает управляемый диффузией рост кристаллов и скорость роста кристаллов понижается.

Рис. 1. Зависимость стандартного отклонения среднего размера микрочастиц от времени нагрева при постоянной температуре 900 °C; ● — Li₂TiO₃, △ — CaTiO₃, ○ — SrTiO₃.

Рис. 2. SEM микросъемки порошкового Li₂TiO₃, приготовленного при температуре 900 °C во время 4 часов.

Рис. 3. SEM микросъемки порошкового CaTiO₃, приготовленного при температуре 900 °C во время 4 часов.

Рис. 4. SEM микросъемки порошкового SrTiO₃, приготовленного при температуре 900 °C во время 3 часов.

RADIOACTIVE WASTE FORMS FOR THE FUTURE (Radioaktivní odpady pro budoucnost). Edited by W. Lutze and R. C. Ewing. North-Holland Physics Publishing, Elsevier Science Publishers, Amsterdam 1988. 778 str.; cena 247,25 US dol.

Kniha přináší přehled nejdůležitějších informací o celém spektru radioaktivních produktů fixace, jež byly vyvinuty nebo alespoň navrženy pro inkorporaci vysoceaktivních jaderných odpadů. Mnoho výsledků bylo publikováno v závěrečných zprávách národních laboratoří nebo v různých, obvykle méně dostupných sbornících. Toto je první publikace, jež shrnuje informace o mediích pro vysoceaktivní jaderné odpady v jednom svazku.

Ačkoliv boritokřemičité sklo se stalo standardním typem materiálu pro tento účel, je nutno v jeho výzkumu dále pokračovat. Se zdokonalením výrobní technologie a s podrobnějšími znalostmi o podmínkách v uložištích mohou být vyvinuta skla a materiály druhé generace se zdokonalenými vlastnostmi. Pokračování výzkumných programů zaměřené na fixační média přinese výsledky, jež jedině mohou zvýšit důvěru veřejnosti v konečné a bezpečné uložení jaderných odpadů. Cílem této knihy je poskytnutí odrazového můstku pro toto budoucí výzkumné úsilí.

V knize jsou podrobně uvedeny vlastnosti a funkce nekystalických produktů (boritokřemičité sklo, spékané sklo, olovnato-železité fosfátové sklo) i produktů krystalických (Synroc, keramika na bázi TiO₂, sklokeramika a beton FUE-TAP). Kapitola o nových formách odpadů uvádí řadu metod, které opodstatňují další vývoj vzhledem k jejich potenciálním vynikajícím vlastnostem a unikátním aplikacím. Závěrečná kapitola uvádí tabelární srovnání důležitých vlastností jednotlivých typů produktů a rozsáhlou diskusi o korozních procesech i o účincích radiace. Zvláštní pozornost je věnována kritickému zhodnocení boritokřemičitého skla a keramiky Synroc. Je to první pokus o podrobné srovnání těchto dvou významných produktů na základě celého souboru jejich materiálových vlastností. Diskuse zdůrazňuje obtížnost takového srovnávání a specifikuje druh dat, jež jsou pro to nezbytná.

Komplexní systémové přístupy vedly v poslední době k částečnému odsunutí role chemické stability odpadů do pozadí. Autoři knihy však dospívají k závěru, že kritickou bariérou pro uvolňování radionuklidů musí zůstat vlastnosti samotného zpracovaného odpadu, protože jeho chování lze snadněji modelovat nežli předvídat dlouhodobé hydrologické a geofyzikální změny v uložištích. Současně je třeba mít k dispozici celou paletu fixačních medií, aby bylo možno inkorporaci radionuklidů optimalizovat s ohledem na složení odpadů i na způsob uložení.

Každá kapitola knihy byla napsána vybranými experty a zahrnuje kompilaci údajů s rozsáhlým seznamem referencí. Kniha představuje stimulační základ pro další výzkum tím, že přináší kritický přehled současného stavu. Kniha bude užitečná nejen pro odborníky v oboru zneškodňování radioaktivních odpadů, ale také v oboru materiálových věd a v oborech skla a keramiky, protože tyto materiály představují hlavní typy fixačních medií.

J. Hlaváč

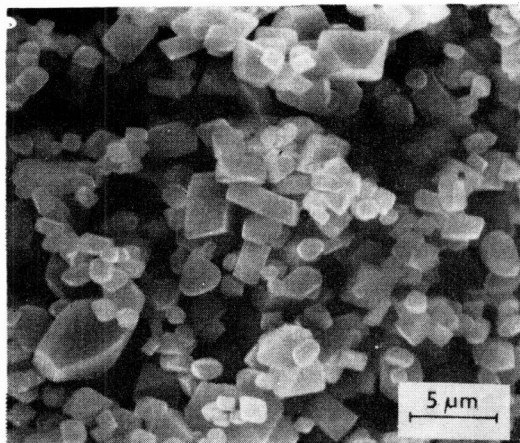


Fig. 2. SEM microphotograph of Li_2TiO_3 powder synthesized at 900°C for 4 h.

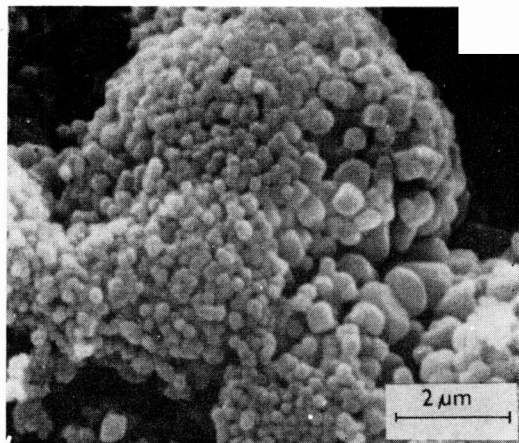


Fig. 3. SEM microphotograph of CaTiO_3 powder synthesized at 900°C for 4 h.

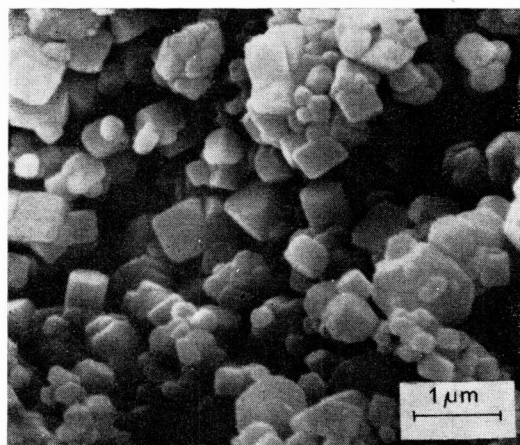


Fig. 4. SEM microphotograph of SrTiO_3 powder synthesized at 900°C for 3 h.