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Fabrication of Li_2TiO_3 spherical microparticles from $TiCl_4$ by a classical, inorganic sol-gel route; characteristics and tritium release properties

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Medium sized spherical particles of Li_2TiO_3 (with diameters below 100 μm) can be fabricated by a classical, inorganic sol-gel process, from commercially available $TiCl_4$. Elaborated process consists of the following main steps: (1) dissolving of $TiCl_4$ in concentrated aqueous HCl; (2) formation of sol emulsion in 2-ethylhexanol-1 containing the surfactant SPAN-80 (EH); (3) gelation of emulsion drops by extraction of water with partially dehydrated EH; (4) impregnation of gel to Li : Ti molar ratio (MR) = 2; (5) thermal treatment at 1200°C. This temperature can be significantly lowered (to 750°C) by chemical treatment of chloride precursors (gels or starting solution $TiCl_4$) with aq. ammonia or better with nitric acid. Tritium release from sol-gel made Li_2TiO_3 micro-spheres were found very close to that observed for other traditional materials, however for the first sample process starts slightly earlier. *© 2002 Kluwer Academic Publishers*

1. Introduction

The world wide actual projects of the future Fusion Reactor (FR) power plants are based on the overall nuclear fusion reaction (1)

$$^6Li + D \rightarrow 2He + 22.4\ MeV \quad (1)$$

The role of the lithium-6 fuel is that of generating tritium by the following $^6Li(n, \alpha)T$ nuclear reaction (2)

$$^6Li + n \rightarrow (He + 2.1\ MeV) + (T + 2.7\ MeV) \quad (2)$$

inside the blanket of the thermonuclear reactor by exploiting the fast neutrons (n) coming out from the D-T fusion (3) as vectors carrying out of the plasma most of the produced energy in this stage

$$D + T \rightarrow (He + 3.52\ Mev) + (n + 14.1\ Mev) \quad (3)$$

Since the fission (2) products (tritons (T) and α particles (He)) will release they energy (4.8 MeV total) inside the blanket, the engineering of the step (2) must provide removal and recovery of both the tritium needed for (3) and of the heat which amount is an important fraction (21.4%) of that of overall process (1).

One of the research lines to make this process (2) feasible for the FR is based on blanket engineering concepts using Li-ceramics in a way similar to that developed for the fission reactor power plants using U-Pu oxide ceramics as fissile fuels. The works performed in the last two decades in this field has been reviewed by Johnson [1] who pointed out the lack of data concerning Li_2TiO_3 as one of the most promising candidate.

Within the frame of Fusion European Program the evolution of the Li-ceramics based blanket design leaded to concentrate the efforts on the "Helium Cooled Pebble Bed" (HCPB) blanket, for which the envisaged Li-ceramics are Li_4SiO_4 (reference material for FzK [2]) or Li_2TiO_3 (under development at CEA [3] with ENEA involved in its re-processing [4]) in form of dense spheres (pebbles) with diameters ranging about 1 mm. These last Li-titanate pebbles are fabricated at size of about 1.2 mm in diameter by the "extrusion-spheronization-sintering" [3] of the powder obtained by the solid state reaction (4).

$$Li_2CO_3 + TiO_2 \rightarrow Li_2TiO_3 + CO_2 \quad (4)$$

The density of the pebbles being optimized to values close to 95% of TD (theoretical density, based on the Li_2TiO_3 single crystal density of 3.43 g/cm^3). The smear density of the pebble bed however cannot exceed the theoretical value of 62% for a packed bed of spheres with near the same radius. Li density is in the fact an important parameter in the economy of FR, an increase in this value leads to a reduction of the lithium-6 enrichment needed to ensure "self-breeding" of the stage (2). A significant increase on the pebble bed density may be obtained by a bimodal distribution of the pebbles size, that is optimized by introducing pebbles with dimension scaling down a factor ten in respect to that characterizing the original one (diameter ∼1 mm), the

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smear density achievable in principle being 88% of TD. So fabrication of dense Li_2TiO_3 spheres with a diameter ranging about 100 μm is an interesting objective for the fusion technology, and the development of a real Sol-Gel process could be the suitable one to achieve it. Years ago this route was tried to obtain $LiAlO_2$ ceramic granules [5]; this material is however not more considered for tritium breeding blankets since Al was discovered to produce long life beta-emitting isotopes under the very energetic (14 MeV) neutron flux from (3). The necessary precursor for sol-gel Li_2TiO_3 microspheres preparation has to be a stable Li and Ti salts aqueous solution, that is difficult to achieve because of the very strong resistance to the acidic attack of TiO_2. Recently Alvani *et al.* [4] where able to completely dissolve Li_2TiO_3 pebbles in commercial hydrogen peroxide (H_2O_2, 40% by volume) at room temperature, the Li-Ti complex solution being stabilized by bidental acetic or citric acid addition. This solution was successfully used [6] in so named IChTJ variant of sol-gel process described in the papers [7, 8] for production of Li_2TiO_3. In this process spherical powders with diameter <100 μm are generally fabricated using extraction of H_2O from inorganic hydroxyl sol's emulsion drops in ethylhexanol (EH) following by thermal treatment.

The aim of this work is to demonstrate the feasibility of a mentioned sol-gel route to prepare Li_2TiO_3 pebbles (from commercial $TiCl_4$) with an average diameter close to 100 μm and to test their tritium release properties by fast Temperature Programmed Desorption (TPD) methods applied to shortly neutron irradiated specimens, with tritium implanted at room temperature by the process (2). As a source of Ti we would like to application of $TiCl_4$, which is practically the one, low price commercial product, commonly used for large-scale production of titanium dioxide.

2. Experimental

Commercial $TiCl_4$ was used for production of spherical particles of TiO_2 (with diameters $<100\,\mu$m) by mentioned sol-gel process [7, 8]. The process consist of the following steps: (1) dissolving of $TiCl_4$ in concentrated HCl to solution of 2 M; (2) preparation of concentrated hydroxide sol ($\sim$3 M.) of Ti of composition $TiO(OH)_{1.7}Cl_{0.3}$ by extraction of chlorides using Primene JMT; (3) formation of sol emulsion in 2-ethylhexanol-1 containing the surfactant SPAN-80 (EH); (4) gelation of emulsion drops by extraction of water with partially dehydrated EH; (5) non-destructive thermal treatment at 900°C.

For preparation of mixed oxides or compounds as for example $LiAlO_2$, via the mentioned above process, salts of cations, are added to sols. Consequently, we decided to introduce into a Ti sol initially LiCl and later LiOH to decrease Cl^- content. Evidently chlorides content in a final ceramic blanket is not allowed. Further experiments confirmed that removing chlorides by thermal treatment of Li-Ti-OH-Cl gels is a relatively difficult problem. Consequently, we elaborated an alternative chemical removing procedure of chlorides from these spherical powders.

Potentiometric titrations were carried out with a Labor-pH-Meter, Knick-type 646/647/647-1 using Ingold combined electrodes. Sols were sometimes prepared and concentrated under vacuum using a Buchi RE 121 Rotavapor. In this equipment impregnation of Li deficient gels and chemical dechlorination of samples have been carried out. The viscosity of sols was measured using Ubbelohde capillaries.

Gels and the products of their thermal treatment (in a programmed Carbolite furnace type CSF 1200) were characterized by the following methods:

- thermal analysis (TG, DTA) using a Hungarian MOM Derivatograph (sample weight—200 mg, heating rate—10°C/min., atmosphere—air, static, reference material—Al_2O_3, sensitivity: TG-200, DTG-1/5, DTA-1/5),
- X-ray diffraction (XRD), Cu K_α (Philips Diffraction System).
- SEM using a scanning electron microscope (Zeiss DSM 942).

Li, Ti and chlorides in gels were determined analytically. Li and Cl in calcined products were evaluated by those determinations in aqueous solution obtained by leaching with water.

The Li-ceramics tritium release testing was performed by TPD methods as described in details in [9].

3. Results and discussion

Sol Ti, white in color, prepared by extraction of anion from $TiCl_4$ aqueous solution (150 g Ti/l, Cl : Ti molar ratio, MR $\sim$4 : 1) has very low pH < -0.7, MR Cl : Ti $= 0.5$ and concentration 200 g Ti/Cl. This indicates that together with chloride anion water is extracted. Because extraction process is relatively laborious and pH obtained very low we tried to prepare Li-Ti sols directly by neutralization $TiCl_4$ aqueous solution with 4.5 M LiOH. Potentiometric titration curve, shown in Fig.1, indicates that white sols without precipitation, can have MR of Li : Ti more 3 : 1.

For preparation larger quantities of sols stoichiometric volume, LiOH was sucked to $TiCl_4$ solution into bulb in Rotavapor. The resulting sol concentration of

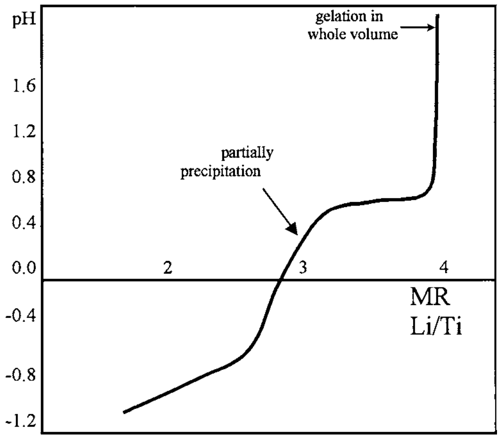


Figure 1 Potentiometric titration curve of $TiCl_4$ aqueous solution with LiOH.

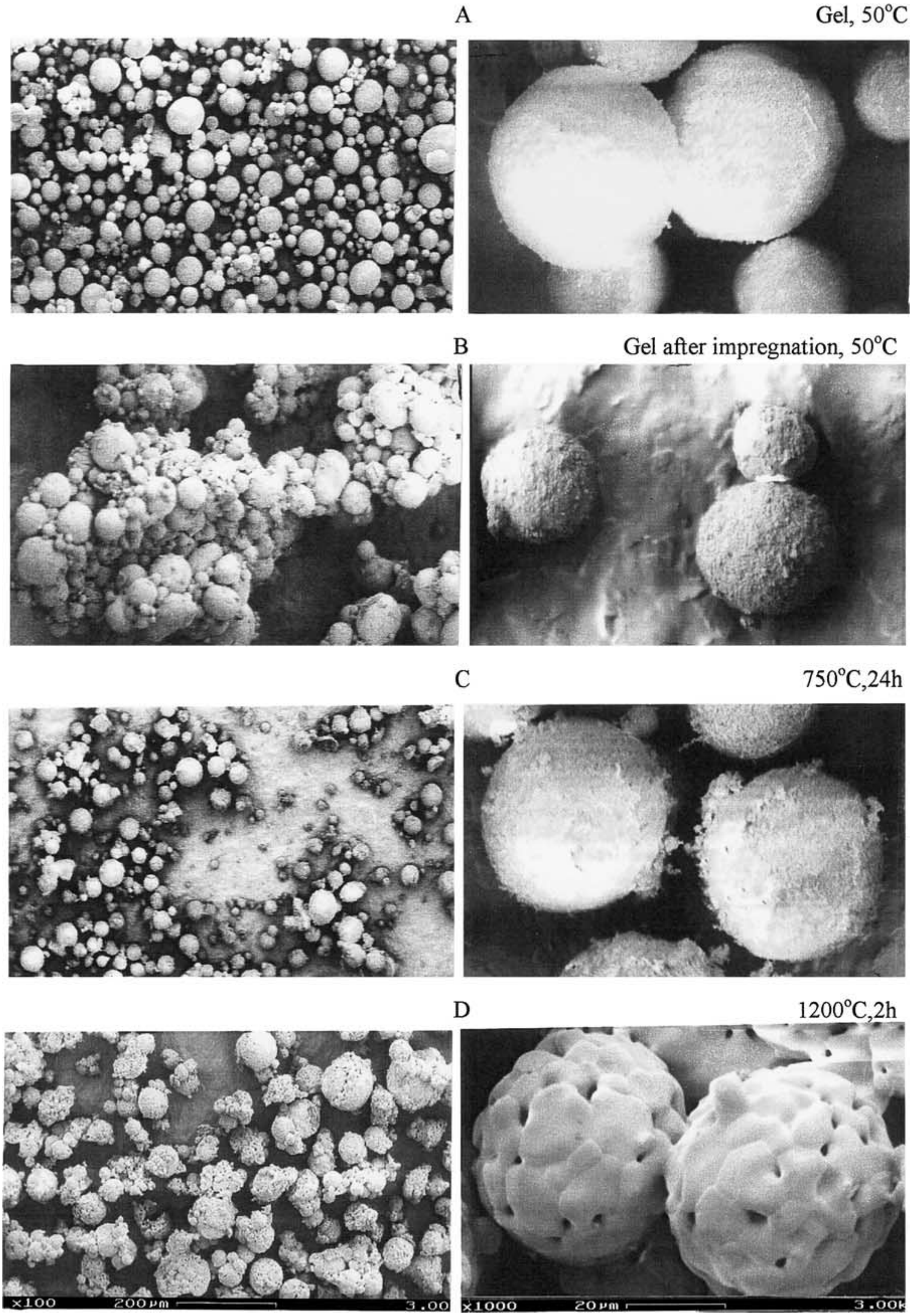


Figure 2 SEM photomicrographs of spherical particles of Li-Ti gel and Li_2TiO_3 obtained in various steps from $TiCl_4$ solution.

~1 M Ti has relatively low viscosity 2 cSt, too low for the next step being the gelation to microspheres [7, 8]. Consequently, sols were concentrated under vacuum approximately 4 times in a volume to viscosity >10 cSt. Concentrated sols were stable for several days.

Sols were than gelled to spherical particles (Fig. 2A). Unfortunately after the process MR of Li : Ti decreased to value ~0.3, presumably due to extraction by EH of Li chloride, together with water. In order to prepare a stoichiometric gel we applied an impregnation process

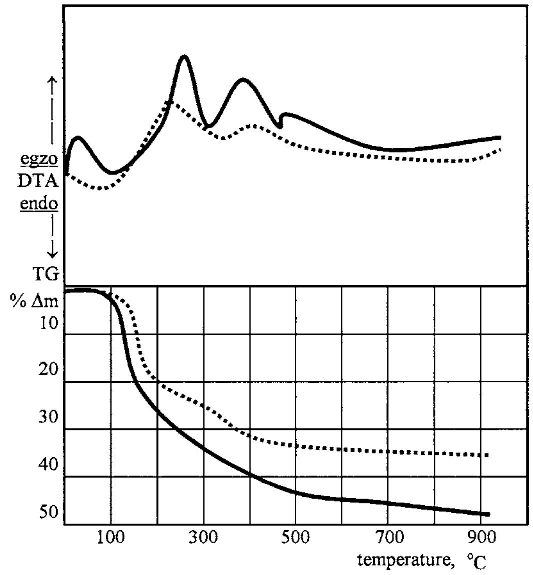


Figure 3 Thermal decomposition of Li-Ti gel before and after impregnation. ———— gel before impregnation, 50°C, 22 h; .... gel after impregnation, 50°C, 2 h (vacuum).

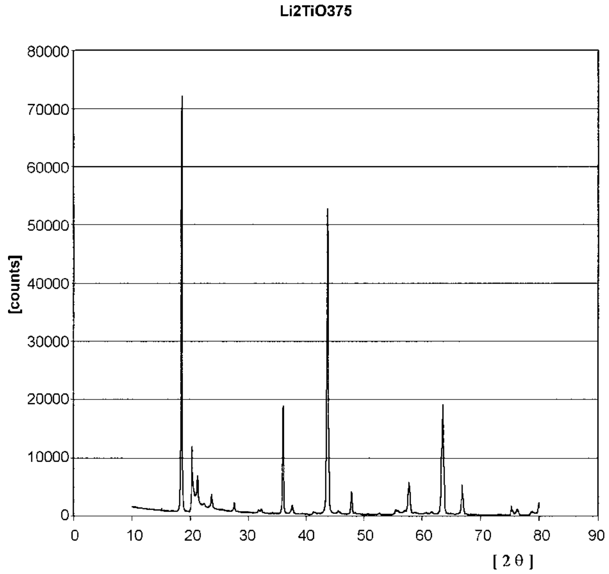


Figure 4 X-ray diffraction plots for Cl^- containing Li_2TiO_3 precursor heated at 750°C for 24 h.

used for spherical powders [8]. The desired quantity of LiOH solution was introduced into gel microsphers placed in Rotavapor. It was observed (Fig. 2B) that after water evaporation the shape of microspheres remained unchanged.

The thermal decomposition of both gels is shown in Fig. 3. It can be seen that the weight loss is lower for the impregnated gel. After similar exothermic effect also weight stabilization after 700°C is more effective for the impregnated gels. Unfortunately, after calcination at 750°C considerable quantities (∼20%) of chlorides remained in a product. The chlorides are presumably homogeneously distributed, because LiCl bands are not observed in XRD patterns (Fig. 4).

Further thermal analysis of this material, shown in Fig. 5, confirmed this conclusion. Final weight stabilization with endothermic effect is observed in 1200°C with a weight loss which corresponds with loss of chlorides. This temperature is significantly lower than the temperature of sublimation of LiCl (1383°C). XRD results (Fig. 6) confirmed that at 1200°C lithium titanate is present and chlorides content is very low (<0.03%) comparable with the quantities (0.02%) introduced to synthesis with LiOH (Fluka p.a. 0.01%Cl) applied in our work.

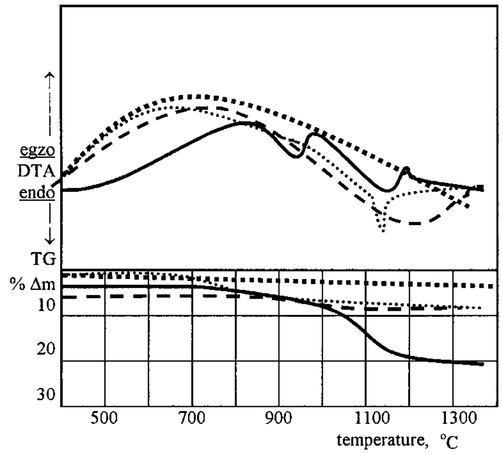


Figure 5 Thermal decomposition of various Li_2TiO_3 precursors. ———— Li_2TiO_3 (Cl) precursor, 750°C, 1 h; – – – – Li_2TiO_3 precursor treated with NH_4OH, 750°C, 24 h; ....Li_2TiO_3 precursor treated with HNO_3, 750°C, 24 h; .... Li_2TiO_3 precursor from HNO_3 stabilized titania sol, 750°C, 24 h.

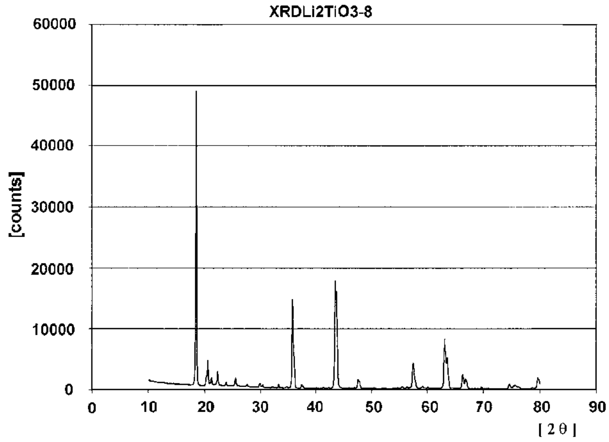


Figure 6 XRD patterns of Li_2TiO_3 obtained from Cl precursor at 1200°C for 2 h.

In order to lower the temperature of formation we carried out the following experiments to remove chlorides in various stages of a process:

I. Gel precursor containing chlorides, heated at 750°C was treated with aq. ammonia and water from slurry was evaporated to obtain a solid. After thermal treatment at 750°C only small quantities of Cl (∼1%) were found and XRD data confirm lithium titanate structure (Fig. 7). It confirms that during heating NH_4Cl undergo sublimation (T.s. 338°C). Thermal analysis (Fig. 5) of dechlorinated material has shown that practically no weight loss in temperature range 900–1200°C was observed during removal of chlorides (see Fig. 5). Evidently thermal effects are absent.

II. Gel precursor heated at 750°C was treated in Rotavapor with concentrated HNO_3 and evaporated under vacuum. The process was repeated a few times

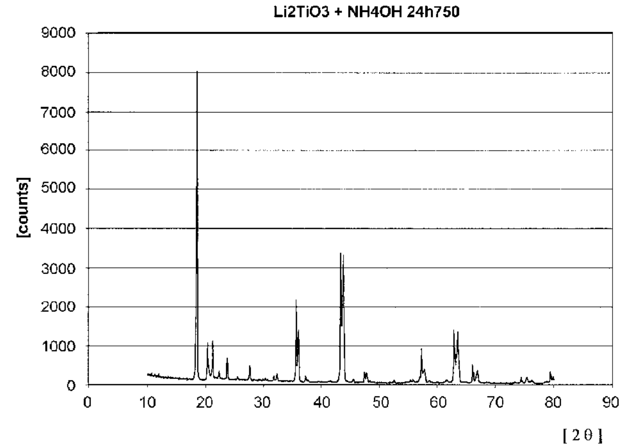
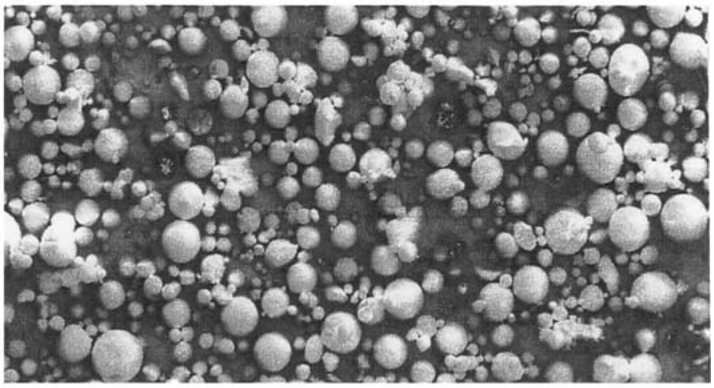


Figure 7 XRD patterns of Li_2TiO_3 obtained at 750°C for 24 h from Cl precursors treated with NH_4OH.

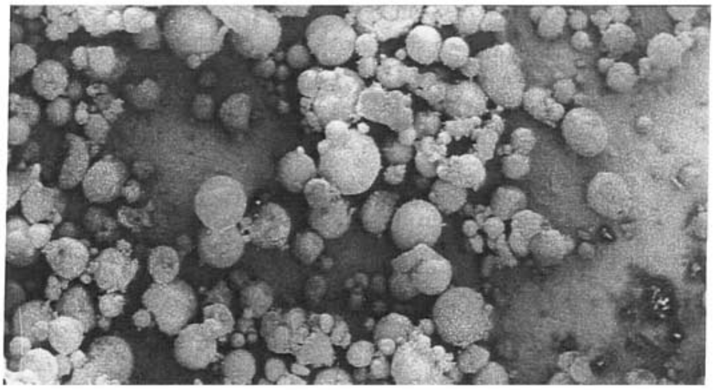
(generally 4) until chlorides were not longer observed in the evaporated solution. Chemical analysis (Cl <0.04) as well as thermal analysis (Fig. 5) indicated that this procedure is more effective than (I). XRD patterns was identical as shown in Fig. 7.

III. Starting aqueous solution of $TiCl_4$ was treated with concentrated HNO_3 in a similar way as described above in (II). Concentrated solution TiO^{2+} nitrate (∼200 g Ti/l), white in color, was prepared. To this solution LiOH can be introduced easily to MR $Li : Ti = 2$, $pH = 0.4$. In higher pH precipitation takes place. Stoichiometric 2Li-Ti nitrate sol, after concentration in Rotavapor (concentrated sol: 230 g/l, viscosity 15 cSt) was gelled to microspheres and than supplied routinely to impregnation. Results of the thermal analysis of precursor heated at 750°C (Fig. 5) as well as content of chloride are similar as observed for the previous material.

Gel, 50°C



Gel after impregnation, 50°C



750°C,24h

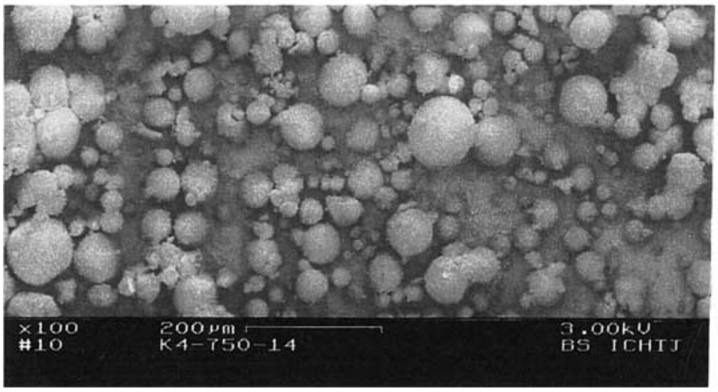


Figure 8 SEM photomicrographs of Li_2TiO_3 spherical particles prepared from Li-Ti-NO_3 sol in various steps of production.

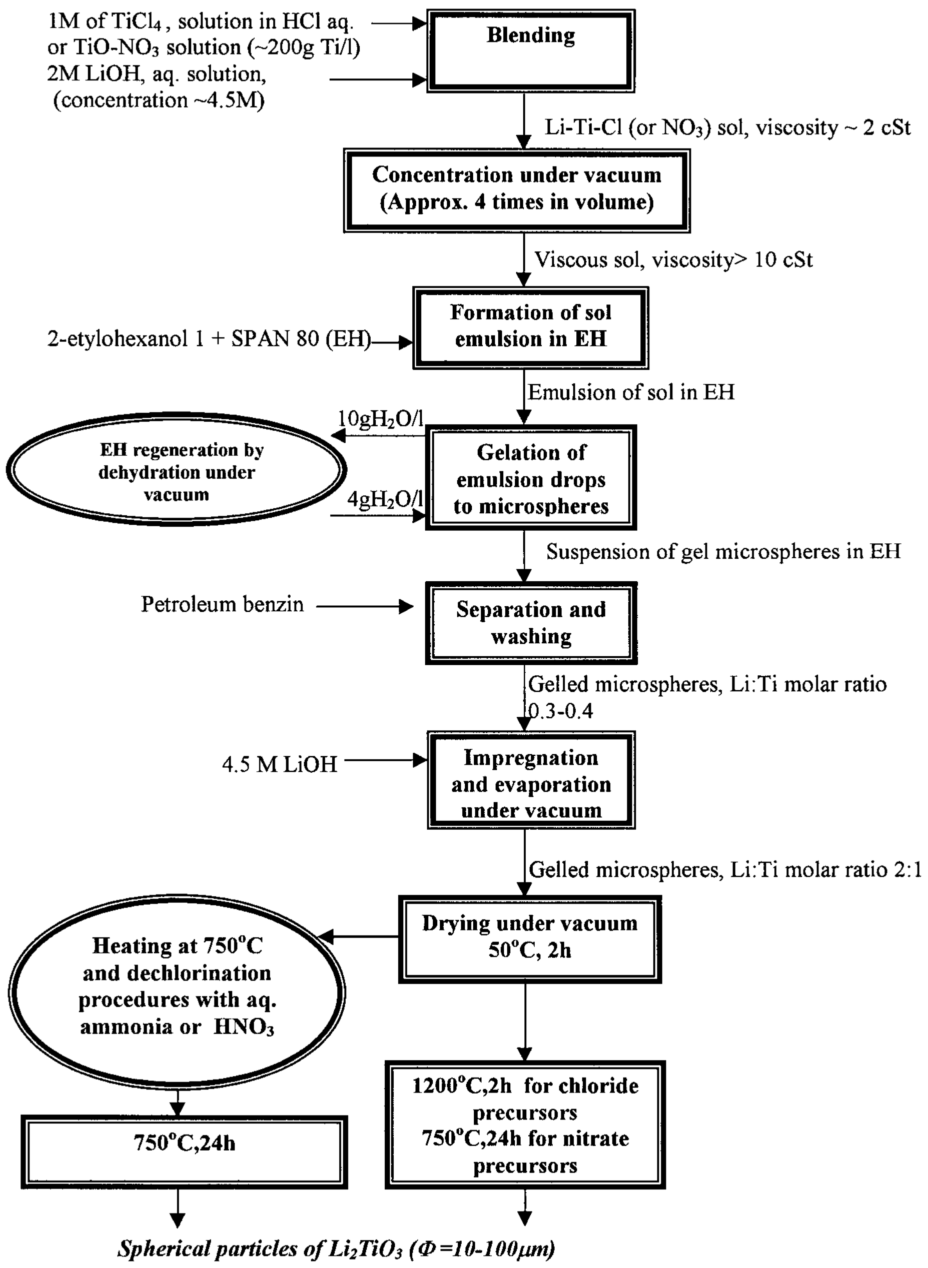


Figure 9 Flow-chart for preparation of spherical powders of Li_2TiO_3 by the sol-gel process.

XRD patterns was identical as shown in Fig. 7. Micrographs of microspheres in various stages of fabrication are shown in Fig. 8.

These results indicate that the effective possibility of chemical, low temperature removal of chlorides from Ti-Li-Cl systems exists. All the described procedures do not change the spherical shape of particles.

The above processes of fabrication of Li_2TiO_3 medium size microspheres (with diameters below 100 μm) are shown in Fig. 9. It is necessary to underline [9] that the formation of medium sized microspheres is practically not possible by powders agglomeration processes routinely used for pebbles fabrication.

Our preliminary experiments indicated that the described variant of sol-gel can be easily used for preparation of other titanates (e.g. $Li_4Ti_5O_{12}$, $BaTiO_3$) or irregularly shaped powders by evaporation of Li-Ti-NO_3 sols and thermal treatment of resulting gels (European patent pending, 2001).

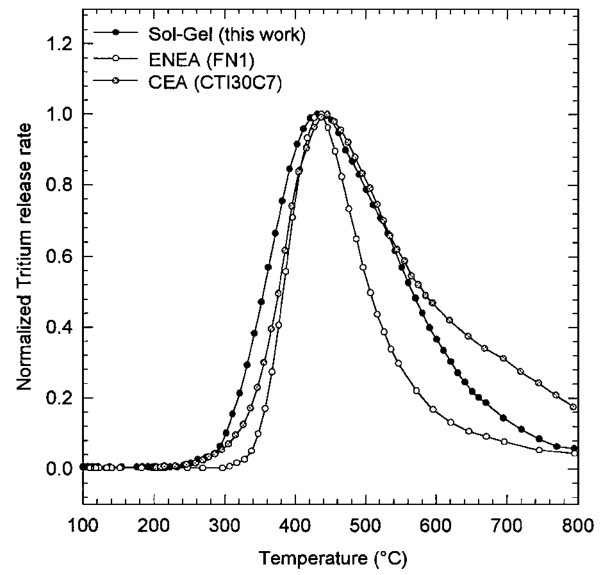
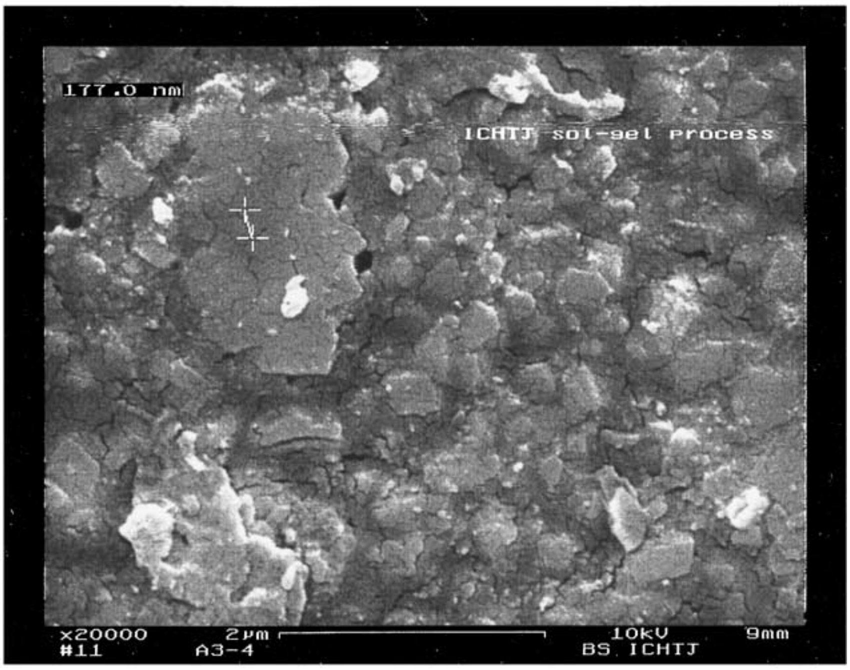


Figure 10 Out of pile TPD tritium release rate from different Li_2TiO_3 samples (heating rate 5°C/min).

Sol-gel (this work)



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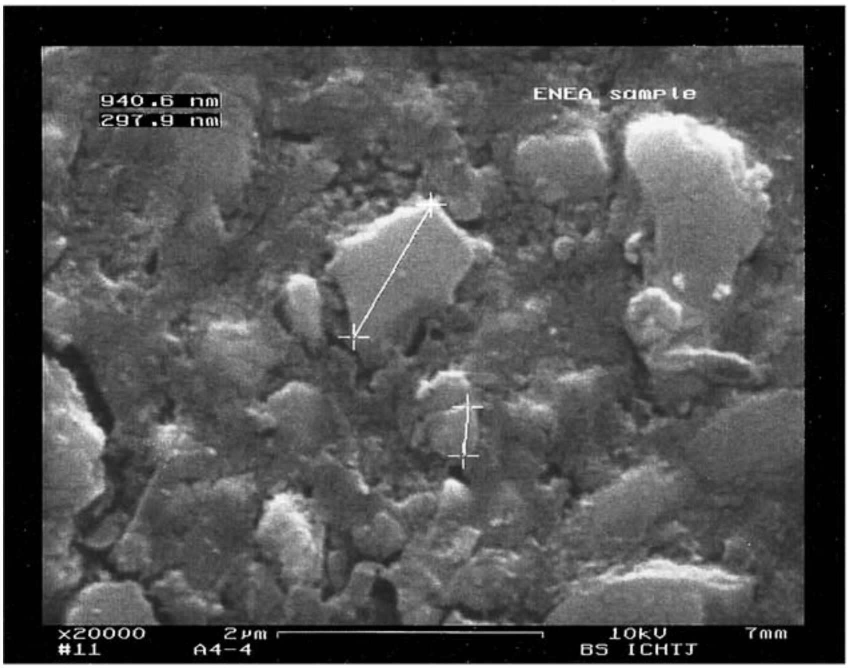

Figure 11 SEM photomicrographs of polished cross section of sol-gel and ENEA samples Li_2TiO_3 (see Fig. 10) used for tritium release rate measurements from different Li_2TiO_3 samples.

Results of preliminary tests of tritium release rate from various type of blankets are shown in Fig. 10. Performance of the sol-gel made Li_2TiO_3 (sample III, Fig. 8) micro-spheres were found very close to that observed for other materials, however for the first sample process starts slightly earlier. It seems that it could be connected with morphology of specimens. Polished cross section (Fig. 11) indicates evidently lower grain size and more interconnected pores. Results of the tritium release indicate moreover that avoids to introduce important modification in the tritium recovery modeling from the blanket in which a bimodal, more dense (∼88%TD) pebble bed in respect of the actual unimodal [1].

4. Conclusions

1. Medium sized spherical particles of Li_2TiO_3 (with diameters below 100 μm) can be fabricated by classic, inorganic sol-gel process from commercially available $TiCl_4$. Impregnation of gels to Li : Ti molar ratio = 2 is necessary. Scaling up from laboratory to pilot plant 1 kg/h level seems to be possible.

2. Full removal of harmful chlorides can be carried out by thermal treatment of Cl containing precursors at 1200°C.

3. This temperature can be lowered (to 750°C) by chemical treatment of chloride precursors (gels or starting solution $TiCl_4$) with aq. ammonia or better with nitric acid.

4. The described variant of sol-gel can be easily used for preparation of other titanates (e.g. $Li_4Ti_5O_{12}$, $BaTiO_3$) or irregularly shaped powders by evaporation of Li-Ti-NO_3 sols and thermal treatment of obtained gels.

5. The feasibility of a sol-gel route to produce Li_2TiO_3 micro-spheres with a diameter ranging about a factor ten less than the actual size of the "extruded-spheronized-sintered" pebbles, allowing in principle an increase in the smear density of the bed hence in the lithium density in the FR blanket, without any apparent modification in the tritium release properties of the pebble bed as purged by s slowly flowing $He + H_2$ (0.1%) gas carrier.

6. Tritium release process starts slightly earlier for sol-gel samples what could be connected with morphology of specimens.

References

1. C. E. JOHNSON, *J. Nuclear Mat.* **270** (1999) 212.
2. E. V. BOCCACCINI *et al.*, Proceedings of 20th SOFT, 7–11 September 1998, Marseille, France, Fision Technology 1998, edited by B. Beaumont, P. Libeyre and G. Tonon (CEA-Cadarache), p. 1255.
3. J. D LULEWICZ and N. ROUX, Proceedings of 7th International Workshop on Ceramic Breeder Blanket Interactions, edited by Jaan van der Laan (NRG), Petten, The Netherland, 14–16 September 1998, p. 5–11.
4. C. ALVANI *et al.*, European Fusion Technol. Progr., HCPB Blanket (Unit B). ENEA report Doc. INN/NUMA/MATAV(99) 1.
5. C. ALVANI, S. CASADIO, L. LORENZINI and G. BRAMBILLA, *Fusion Technology* **10** (1986) 106.
6. C. ALVANI, P. L. CARCONI, S. CASADIO, A. DEPTUŁA and S. LAGOS, *J. Nucl. Mat.* **289** (2001) 303.
7. A. DEPTUŁA, J. REBANDEL, W. DROZDA, W. ŁADA and T. OLCZAK, in "Better Ceramic Through Chemistry V," edited by M. J. Hampden-Smith, W. G. Klemperer and C. J. Brinker (Mat. Res. Soc. Symp. Proc. 270, Pittsburgh, PA, 1992) p. 277.
8. A. DEPTULA, A. G. CHMIELEWSKI and T. E. WOOD, 9th CIMTEC Proceedings, edited by P. Vincenzini, Florence 1998, Italy, Volume D-Getting into the 2000's.
9. C. ALVANI, P. L. CARCONI, S. CASADIO and F. PIERDOMINICI, Proceedings of 7th International Workshop on Ceramic Breeder Blanket Interactions, edited by Jaap van der Laan (NRG), Petten, The Netherland, 14–16 September 1998, p. 694–804.

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