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Fabrication and characterization of Li_3TaO_4 ceramic pebbles by wet process

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ABSTRACT

Lithium-containing ceramics have long been recognized as the tritium breeding materials in the fusion–fission or fusion reactor blanket. Li_3TaO_4 (lithium orthotantalate) pebbles, with high melting point (~1406 °C), good thermal stability, and high thermal conductivity, were fabricated by wet process (freeze–drying) as a new potential candidate of tritium breeder. The diameter of ceramic pebbles is 0.7–1.0 mm, density is over 90% (TD), pore diameter is 1.86 μm (a.v), grain size is 15 μm (a.v), crush load is up to 46.7 N (a.v).

1. Introduction

In fusion–fission or fusion reactor, lithium ceramics are considered as the candidate solid tritium breeders in the blanket, such as Li_2O, γ-$LiAlO_2$, Li_2ZrO_3, Li_2SiO_3, Li_2TiO_3 and Li_4SiO_4. There are some factors to evaluate the tritium breeders used in fusion–fission or fusion reactor as followings [1]:

(a) High lithium content.
(b) Exhibit thermo-physical, chemical, and mechanic stability at high temperature.
(c) High thermal conductivity.
(d) Be compatible with other blanket and structural materials.
(e) Desirable irradiation behavior.

Recently, $LiTaO_3$ has been investigated as another hopeful candidate for tritium breeding material due to its high melting point (1650 °C) and to high thermal conductivity. According to the study of the behaviors of hydrogen isotopes in $LiTaO_3$ [2], it has been predicted that $LiTaO_3$ may have higher tritium release rate and higher fraction of tritium as T_2 than γ-$LiAlO_2$, Li_2SiO_3, Li_4SiO_4 and Li_2TiO_3. However, the content of lithium in $LiTaO_3$ is only 0.22 g/cm^3, even lower than in γ-$LiAlO_2$. So Li_3TaO_4 may be a better alternative because of its higher lithium content (0.46 g/cm^3).

Li_3TaO_4 has high melting point (~1406 °C), good thermal stability (stable between 0 °C and 1400 °C) and high thermal conductivity (4.351 W m^{-1} K^{-1} (17 °C), 2.069 W m^{-1} K^{-1} (700 °C) for 89.8% TD, where TD is the theoretical density) [3]. The neutron cross section of Ta (20.5 barn) is higher than that of Si (0.177 barn), Ti (7.88 barn) and Li (0.0454 barn), which may cause some problems to the waste disposal process and the reduction of tritium breeder ratio. It may be an attracting tritium breeder candidate in fusion–fission or fission reactor. However, no fabrication process and related property researches of Li_3TaO_4 ceramic pebbles as tritium breeder candidate have been reported yet. In this paper, the fabrication process of Li_3TaO_4 ceramic pebbles was carried out and the characteristics of Li_3TaO_4 pebbles were measured.

There are several major methods to prepare the lithium ceramic pebbles: sol–gel [4], extrusion–spheronization–sintering [5], agglomeration–sintering [6], melting–spraying [7] and wet processes [8,9]. The basic properties of the lithium ceramic pebbles used in ITER blanket should satisfy the needs of China Test Blanket Module (CH TBM) design: small diameter (0.5–1.0 mm), high density (>80% TD), small grain size, micro-porous structure, high crush load and material purity [10]. Because of low-density of pebbles made by sol–gel and extrusion–spheronization–sintering methods, of low sphericity of pebbles made by agglomeration–sintering method and of high cost of pebbles made by melting–spraying method, wet process was considered. Wet process is clean, cheap and more applicable. So wet process (freeze–drying) was adopted in this paper to fabricate Li_3TaO_4 pebbles from the Li_3TaO_4 powder prepared by classic solid-state reaction method (700 °C for 20 h, 800 °C for 100 h, 1000 °C for 20 h) [11]:

$$Li_2CO_3 + Ta_2O_5 \rightarrow Li_3TaO_4 + CO_2 \uparrow .$$

2. Experiment

2.1. Preparation of the Li_3TaO_4 powder

Li_2CO_3 (purity: 99.99%, wt.%) and Ta_2O_5 (purity: 99.99%, wt.%) powder serve as the starting materials to prepare Li_3TaO_4 powder by solid-state reaction method. The starting materials were

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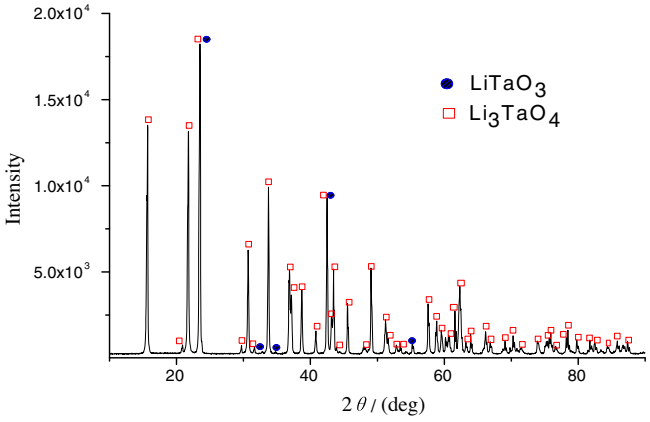

Fig. 1. XRD pattern of the powder sample.

calcinated at 700 °C for 20 h, 800 °C for 100 h, and 1000 °C for 20 h. XRD pattern of the powder sample (Fig. 1) shows that there are two compositions: β-Li_3TaO_4 (major) and $LiTaO_3$ (minor). The phase purity can be calculated by the WPF (whole pattern fitting) refinement in the Jade 6.5 software [12]. Quantitative analysis result is as follows:

- β-Li_3TaO_4 wt.% = 99.1.
- $LiTaO_3$ wt.% = 0.9.
- *R* (residual error function) = 9.88%.

Because there are several stable phases including $LiTaO_3$ and Li_3TaO_4 in Li–Ta–O system, small amount of $LiTaO_3$ was unavoidably produced during the reaction between the Li_2CO_3 and Ta_2O_5.

2.2. Fabrication process

Wet process was used to fabricate Li_3TaO_4 pebbles. The starting material was Li_3TaO_4 powder, which was prepared in our laboratory by solid-state method. To gain the ceramic pebbles with small grain size, the Li_3TaO_4 powder was milled to 1.4 μm (a.v). The fabrication steps are shown as follows:

(a) *Milling*: Polyvinylalcohol (PVA) solution and anti-foam agent were added into the starting materials, and then ball milled to form the homogeneous liquid mixture.
(b) *Fabrication of spheres:* The as-prepared mixture was dropped into the liquid nitrogen (−195 °C) through a nozzle to generate the spheres, and then the spheres were freeze-dried in the freeze dry system.
(c) *Calcination of spheres:* The spheres were calcinated at 500 °C in air to remove PVA and anti-foam agent. Then the low-density Li_3TaO_4 spheres could be obtained.

Table 1
Weight loss of the pebbles after calcination.

Content of PVA (wt.%)	Solid/liquid ratio (wt.%)	Calcination		Weight loss (%)
		Weight of pebbles before calcination/g	Weight of pebble after calcination/g	
4.2	65:35	3.66333	3.57248	2.48
		11.80710	11.51310	2.49
5.78	68:32	4.67996	4.54359	2.91
		16.20907	15.73032	2.95
7.78	68:32	4.02514	3.87581	3.71
		13.13893	12.64638	3.74

Weight of pebbles were measured by scale (XS205 *d* = 1/100,000).

(d) *Sintering*: The low-density Li_3TaO_4 spheres were sintered in air at high temperature (>1000 °C), and the Li_3TaO_4 ceramic pebbles with high density may be attained.

Three experiments were conducted. In the 1st experiment the solid/liquid ratio (Li_3TaO_4 powder/PVA solution) was varied to investigate the influence of the solid/liquid ratio on the sphericity of pebbles. In the 2nd experiment the calcination conditions were examined to remove PVA and anti-foam agent. In the 3rd experiment the sintering temperature and time were varied to observe the effect on the pebble density, diameter, crush load and microstructure.

2.3. Characterization of Li_3TaO_4 ceramic pebbles

The characterization of ceramic pebbles was investigated by using the methods described as follows. The diameter and density were measured by sample survey (digital vernier caliper and scale). The microstructure was studied by scanning electron microscopy (SEM). The crush load was measured by using an unconfined compression tester. The lithium content and pore size of the ceramic pebbles were investigated by atomic emission spectrometry with inductively coupled plasma atomic emission spectrometry (ICP-AES) and mercury intrusion method, respectively. The sphericity was studied by photographic analysis.

3. Results and discussions

3.1. Solid/liquid ratio

PVA served as a binder in the fabrication process of Li_3TaO_4 pebbles. PVA solution was added into the Li_3TaO_4 powder to form the homogeneous liquid mixture, and the solid/liquid ratio could influence the sphericity of pebbles. In the 1st experiment different solid/liquid ratios were studied. When the solid/liquid ratio was less than 55%:45% (wt.%) or more than 70%:30% (wt.%), it would generate irregular or elliptical shapes but not spheres (Fig. 2). For

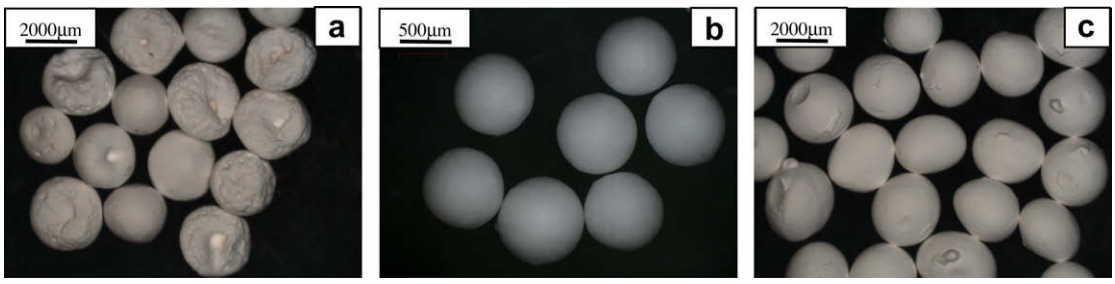

Fig. 2. The morphology of the Li_3TaO_4 pebbles: (a) solid/liquid ratio: 50%:50% (calcinated at 500 °C for 6 h, but un-sintered); (b) solid/liquid ratio: 68%:32% (calcinated at 500 °C for 6 h, and sintered at 1150 °C for 12 h; (c) solid/liquid ratio: 75%:25% (calcinated at 500 °C for 6 h, but un-sintered).

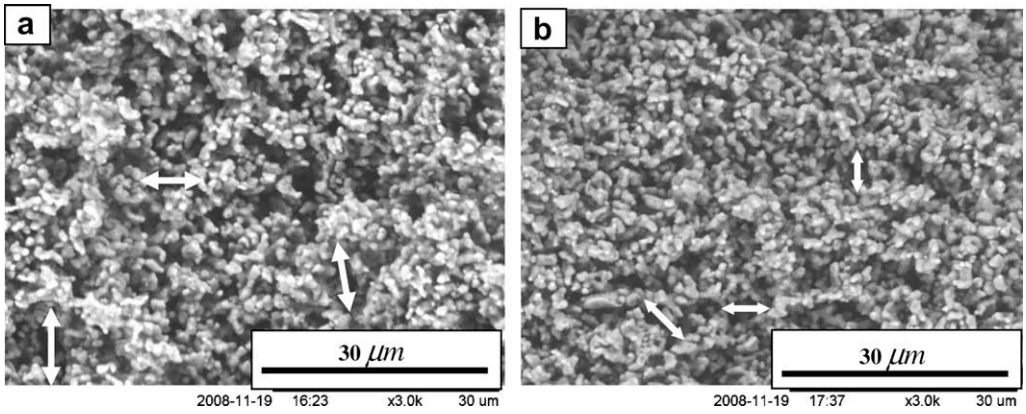

Fig. 3. SEM photographs of pebbles: (a) Li_3TaO_4 pebble before calcination; (b) Li_3TaO_4 pebbles without PVA and anti-foam agent (calcinated at 500 °C for 6 h).

Table 2
Characterization of sintered pebbles.

Sintering temperature (°C)	Sintering time (h)	Diameter[a] (mm)	Sphericity[b]	Density[c] (TD %)	Grain size[a] (μm)	Crush load[a] (N)	Pore size[a] (μm)
1100	12	0.92	1.01	63.2	5	18.4	1.57
1150	6	0.86	1.01	84.8	10	32.5	1.44
1150	12	0.83	1.01	92.1	15	46.7	1.86
1200	12	0.82	1.01	93.0	>20	14.4	2.67

[a] Average.
[b] Sphericity = (d1/d2 + d2/3 + d1/d3)/3, d1 > d2 > d3 – diameter of a pebble, and two of them are orthogonal.
[c] The theoretic density of Li_3TaO_4 is 5.87 g/cm^{-3} [13].

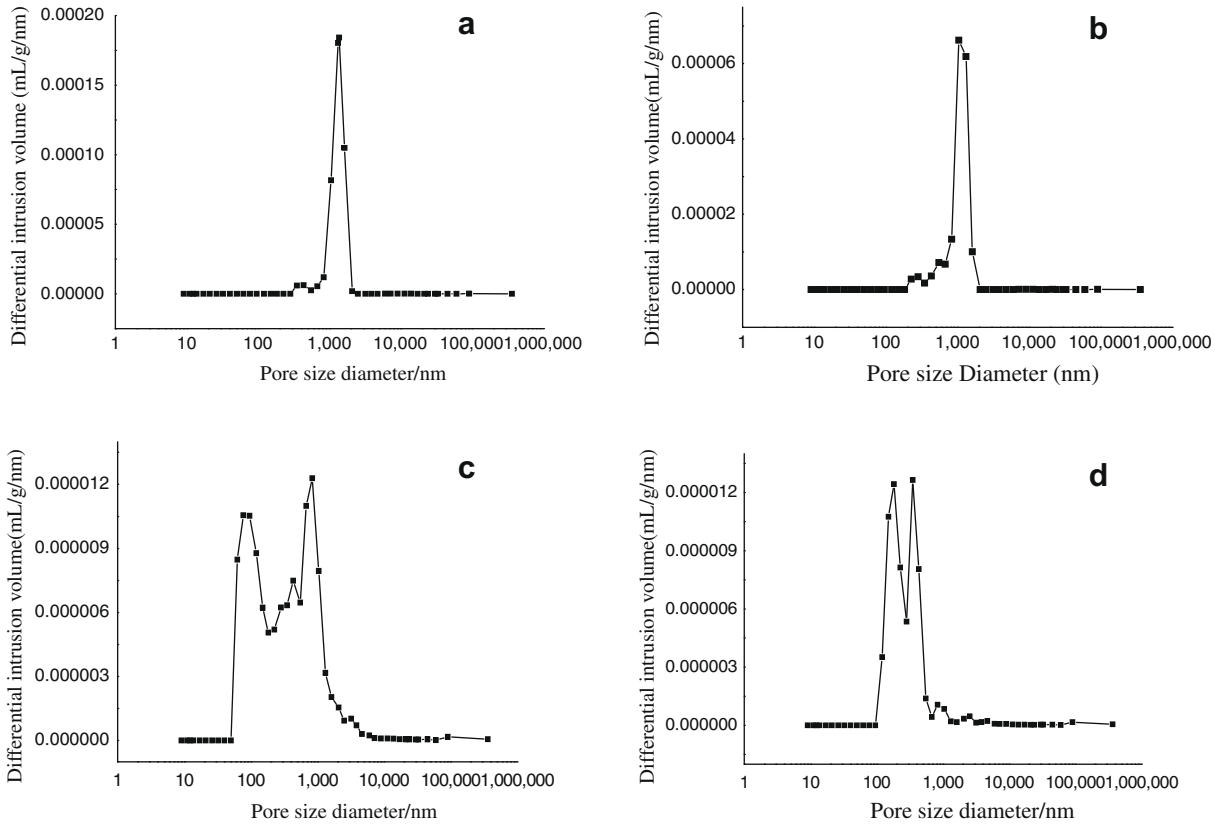

Fig. 4. Pore size distribution of Li_3TaO_4 ceramic pebbles sintered at different temperatures: (a) sintered at 1100 °C for 12 h; (b) sintered at 1150 °C for 6 h; (c) sintered at 1150 °C for 12 h; (d) sintered at 1200 °C for 12 h.

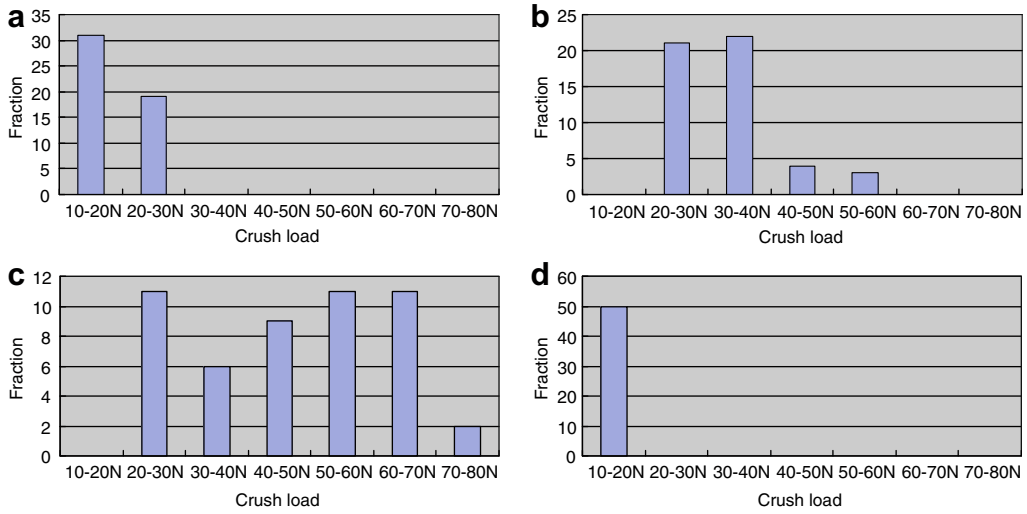

Fig. 5. Crush load distribution of Li_3TaO_4 ceramic pebbles sintered at different temperatures: (a) sintered at 1100 °C for 12 h; (b) sintered at 1150 °C for 6 h; (c) sintered at 1150 °C for 12 h; (d) sintered at 1200 °C for 12 h.

Li_3TaO_4, the preferred content of the Li_3TaO_4 powder was 55–70% (wt.%) (PVA solution: 30–45% wt.%).

3.2. Calcination process

Calcination was carried out to eliminate PVA and anti-foam agent. In the second experiment, different length of calcination time was investigated at 500 °C. PVA and anti-foam agent could be basically removed after heating for 6 h at 500 °C in air. The color of spheres changed to light grey after calcination, and there was certain weight loss. The weight loss for varying amount of PVA and of solid/liquid ratio is shown in Table 1. There are a number of important parameters associated with the calcination process as temperature, duration of time, atmosphere, etc., here only the duration of time is investigated. In order to investigate the effect of calcination time on the crush load of ceramic pebbles, the calcination time was further extended to 12 h, 24 h and 48 h. Then the pebbles were sintered at 1150 °C for 12 h. Finally, the crush load of these pebbles was examined. No obvious influence was observed.

SEM observations were employed to check if the calcination process could lead to grain growth. The comparison of the Fig. 3a (SEM photograph of pebble before calcination) and Fig. 3b (SEM photograph of pebble after calcinated at 500 °C for 6 h) indicated that there was no obvious grain growth, but that the intervals between the grain clusters were shortened (Fig. 3). The spheres after removing PVA and anti-foam agent were sintered at higher temperatures and the Li_3TaO_4 ceramic pebbles of high density could be obtained.

3.3. Sintering process

Sintering temperature is a crucial parameter to optimize the characteristics of ceramic pebbles such as density, crush load, grain size and porosity. It was aimed to gain the pebbles with small diameter (<1.0 mm), high density (>90% TD), high crush load (>40 N) and certain numbers of pores. In the 3rd experiment three sintering temperatures were investigated, 1100 °C, 1150 °C and 1200 °C.

With the sintering temperature increasing from 1100 °C to 1200 °C, the diameter and porosity of pebbles decreased, the density and crystal grain increased (Table 2), the pore size distribution became much broader (Fig. 4). From 1100 °C to 1150 °C the crush load increased, but from 1150 °C to 1200°C the crush load decreased (Fig. 5). SEM photographs showed that the crystal grain grew from about 5 μm to 15 μm when the sintering temperature was increased from 1100 °C to 1150 °C (Fig. 6a and c). When the pebbles were sintered at 1200 °C, the crystal grain size increased more drastically and more pores collapsed (Fig. 6d). This was an over-sintered state. What's more, with the temperature increasing from 1100 °C to 1150 °C, the pores on the surface were partly closed (Fig. 6a1 and c1), but there were a great many pores inside the pebbles (Fig. 6a2 and c2). At 1200 °C, most of the pores on the surface had been closed (Fig. 6d1), and there were some cracks here on the surface, which could lead to the decrease of crush load. But inside the ceramic pebbles pores still existed, which seemed to be closed pores (Fig. 6d2). Closed pores are not in favor of the safety consideration. Because when the pores on the surface are closed and not linked to the pores inside the pebbles, the tritium released in the ceramic pebbles cannot find a way out and would be accumulated inside the ceramic pebbles, which will lead to the low tritium inventory. From the consideration of the pebble size, density and the crush load, 1150 °C had been chosen as the optimum sintering temperature.

Then the sintering time was also investigated. The spheres were sintered at 1150 °C for 6 h and 12 h, respectively. It could be observed the apparent grain growth from 10 μm for 6 h to 15 μm for 12 h (Fig. 6b and c). But the crush load and density of ceramic pebbles increased (Table 2). It is aimed to obtain the ceramic pebbles with high density, small grain size and high crush load. However, the sintering experiments at different temperatures and times exhibited controversial results. The density and the grain size of pebbles increased with temperature and time in favor of the expectation but the crush load did not follow this trend (Fig. 7). Which sintering time of 6 h or 12 h should be adopted has not been decided, because the grain size may be related to the mechanism whether the tritium release rate is decided by diffusion process or by surface reactions (absorption, desorption and isotope exchange) [14].

The crush load of pebbles is also affected by the diameter of pebbles. The larger the pebble diameter, the higher the crush load could result. But the diameter of ceramic pebbles should meet the need of CH TBM design, 0.5–1.0 mm. In our laboratory the diameter of ceramic pebbles was controlled between 0.7 mm and 1.0 mm (Fig. 8). The lithium content of pebbles sintered at 1150 °C for 12 h

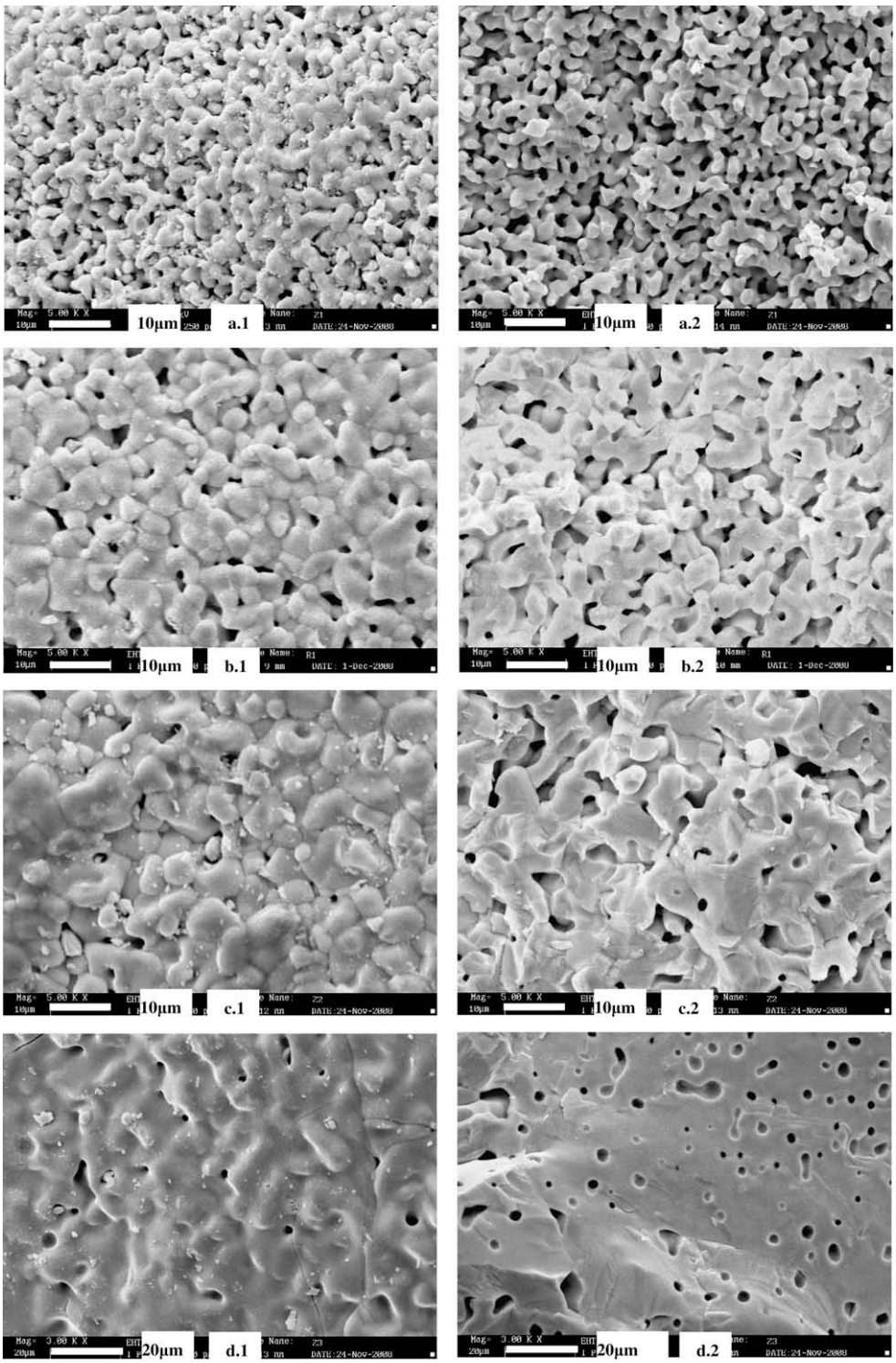

Fig. 6. SEM photograph of the Li_3TaO_4 ceramic pebbles: (a) sintered at 1100 °C for 12 h; (b) sintered at 1150 °C for 6 h; (c) sintered at 1150 °C for 12 h; (d) sintered at 1200 °C for 12 h; (1) surface morphology; (2) cross-section morphology.

was measured by ICP-AES; the lithium content of the ceramic pebbles was 7.8%, close to the formulative content of lithium in Li_3TaO_4 – 7.84%.

4. Summary

Li_3TaO_4 becomes a new attractive candidate of the solid tritium breeder in fusion–fission or fusion reactor blanket because of its high melting point, good thermal stability, and high thermal conductivity.

In this paper Li_3TaO_4 ceramic pebbles were fabricated by wet process (freeze–drying). Several parameters such as solid/liquid ratio, calcination time, sintering temperature and time were optimized as follows:

Solid/liquid ratio: 55%:45%–70%:30% (wt.%).

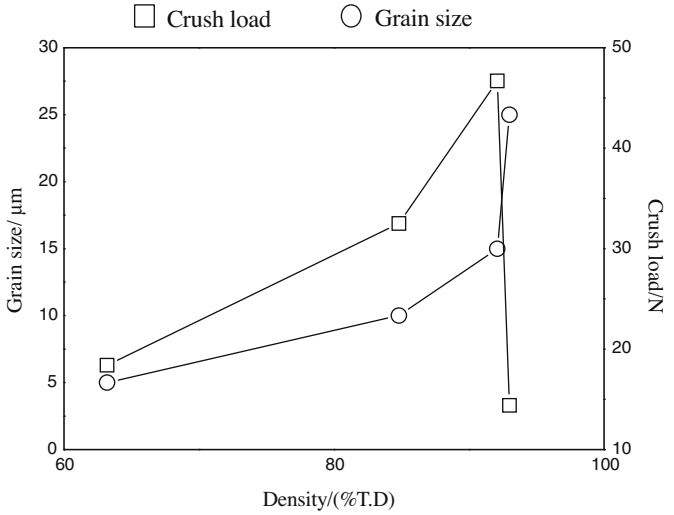

Fig. 7. Relations between the density, grain size and crush load.

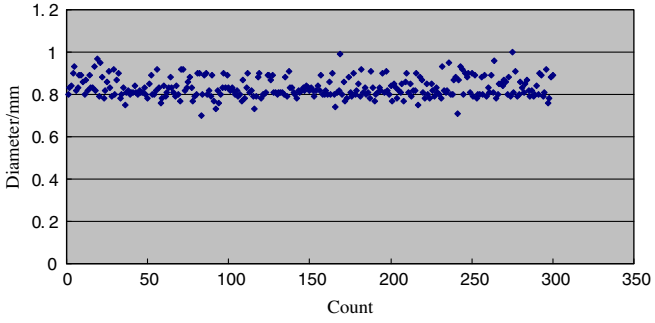

Fig. 8. Diameter distribution of Li_3TaO_4 ceramic pebbles sintered at 1150 °C for 12 h.

Calcination time at 500 °C: 6 h.
Sintering temperature: 1150 °C. (Time is left to be determined.)

Li_3TaO_4 ceramic pebbles with small diameter of 0.7–1.0 mm, large crush load of above 40 N (a.v), density of over 90% (TD), porous structure, small grain size of 15 μm (a.v) and pore diameter of 1.86 μm (a.v) were obtained. As a new candidate of solid tritium breeder in fusion–fission or fusion reactor blanket, further investigations on the tritium release behavior of Li_3TaO_4 including tritium release rate and chemical form of the released tritium should be conducted in the future.

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