Journal of Nuclear Materials 393 (2009) 186–191

Contents lists available at ScienceDirect

Journal of Nuclear Materials

journal homepage: www.elsevier.com/locate/jnucmat

Fabrication and improvement of the density of Li_2TiO_3 pebbles by the optimization of a sol–gel method

Xiangwei Wu, Zhaoyin Wen *, Xiaogang Xu, Jinduo Han, Bin Lin

Shanghai Institute of Ceramics, Chinese Academy of Sciences, 1295 Dingxi Road, Shanghai 200050, PR China

A R T I C L E I N F O

Article history:
Received 24 September 2008
Accepted 2 June 2009

A B S T R A C T

Li_2TiO_3 is regarded as a promising candidate breeder in solid blanket concepts. Pebble configuration has been a preferred option due to its potential advantages in blanket design. Li_2TiO_3 pebbles were successfully fabricated by a water-based sol–gel method previously. However, the sintered density of the pebbles was very low (less than 70% theoretical density). The process parameters were optimized and the sintered density of the pebbles was improved significantly in this work. Li_2TiO_3 pebbles with density as high as 85% were obtained at a relatively lower sintering temperature (1100 °C) and shorter sintering time (4 h). The experimental results showed that the viscosity of the sol was influential to the sphericity of the gel-spheres and thus the sintered pebbles. The variety of lithium source, the pH value of the solution and the sintering conditions demonstrated significant influences on the microstructure and density of the sintered Li_2TiO_3 pebbles.

1. Introduction

Tritium must be generated inside the fusion system to have a sustainable fuel cycle. The most appropriate process to breed tritium is the neutron interaction of lithium containing compounds which have been used in the fusion system in many cases. Lithium titanate, Li_2TiO_3, is considered as one of the most promising candidates for tritium breeding materials in fusion reactors [1,2]. The most common shape of the tritium breeders were usually adopted either as a pebble or pellet. Recently, the pebble configuration has been taken as a preferred option in most blanket designs due to its potential advantages in the assembly of blankets with complex geometry, in the relief of thermal stress and irradiation cracking, and in the diffusion and release of tritium [3,4]. In the blanket design, the characteristics of the pebbles should also meet the following requirements: spherical shape, diameter of about 1 mm, density of approximately 85%T.D. [5].

Several fabrication technologies, including wet process based on powder-gelation or dehydration or substitution reaction [6–8], sol–gel type processes [9–11], the agglomeration/sintering process and the extrusion–spheronization–sintering process [5,12] are available to produce Li_2TiO_3 pebbles. In our previous work, a water-based sol–gel method was established for fabrication of Li_2TiO_3 pebbles [11]. However, the sintered density of the Li_2TiO_3 pebbles was less than 70%T.D. even sintered at the temperature as high as 1200 °C and for sintering time as long as 10 h.

In this work, the water-based sol–gel method was re-examined to improve the density of the pebbles. Lithium hydroxide (LiOH) and lithium acetate (CH_3COOLi) were chosen as the lithium source instead of lithium nitrate ($LiNO_3$), respectively. The influences of the variety of lithium source, the pH value of the solution and the sintering conditions on the density of the sintered Li_2TiO_3 pebbles were systematically studied. Li_2TiO_3 pebbles with density as high as 85%T.D. were fabricated at a relatively lower sintering temperature (1100 °C) and for shorter sintering time (4 h) by the optimized method. The shape of the obtained Li_2TiO_3 pebbles was nearly spherical and the average diameter of the pebbles was 1.24 mm.

2. Experimental procedure

2.1. Fabrication of Li_2TiO_3 pebbles

LiOH and CH_3COOLi were used as the lithium source, respectively. Titanium-containing aqueous solution was prepared according to the method reported previously [11]. However, the molar ratio of tetrabutyl titanate ($Ti(C_4H_9O)_4$) to citric acid ($C_6H_8O_7$) was fixed at 1 instead of 0.5 previously adopted. LiOH was dissolved in distilled water, then citric acid ($C_6H_8O_7$) solution was added to adjust the pH value of the LiOH solution to 6.5–12.5. When CH_3COOLi was chosen as the lithium source, citric acid was not used and the pH value of the CH_3COOLi solution need not to be adjusted. Thereafter, titanium-containing aqueous solution was poured into the above solution to the molar ratio of Li/Ti = 2. The mixture was evaporated at 60 °C until the formation

---

* Corresponding author. Tel.: +86 21 52411704; fax: +86 21 52413903.
E-mail address: zywen@mail.sic.ac.cn (Z. Wen).

0022-3115/$ - see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.jnucmat.2009.06.002

of the sol. The following steps for fabrication of Li_2TiO_3 ceramic spheres were similar to those reported previously [11].

2.2. Characterization

The viscosity of the sol was measured by programmable rheometer (DV III+, BROOKFIELD) at room temperature. Thermal behavior of the gel-spheres was carried out by thermogravimetry (TG) and differential scanning calorimetry (DSC) (NETZSCH 409 PC) in air at a constant heating rate of 10 °C/min in the temperature range of 100–800 °C. Crystallographic phase analyses were conducted by X-ray diffraction (Rigaku RAD-C, 12KW) measurements (Cu Kα). The microstructure of the sintered ceramic spheres was observed by field emission scanning electron microscope (FEI Quanta 200). The sintered density of the Li_2TiO_3 pebbles was tested by Archimedes' principle using ethyl alcohol as the immersion medium.

3. Results and discussion

3.1. Characteristics of the pebbles

Li_2TiO_3 pebbles were prepared at the pH value of the solution of 8.5 by the optimized sol–gel process. The morphology of a batch of Li_2TiO_3 pebbles sintered at 1100 °C for 4 h is presented in Fig. 1. It can be seen from Fig. 1 that the shape of the Li_2TiO_3 pebbles was nearly spherical. However, the surface of the sintered pebbles was uneven because of the uneven surface of the gel-spheres (Fig. 3(b)), which might be resulted from the heterogeneous shrinkage of the gel-spheres during the drying process. The diameter of the pebbles sintered at 1100 °C for 4 h distributed in the range of 1.18–1.30 mm. The density of the pebbles sintered at 1100 °C for 4 h was about 85%T.D., which was much higher than that of the pebbles obtained previously [11].

3.2. Effect of the viscosity of the sol on the morphology of the gel-spheres

The properties of the sol, especially the viscosity, had significant influences on the formation of gel-spheres. Fig. 2 shows the variation of the viscosity as a function of shear rate for the sol prepared at pH 8.5 and using LiOH as the lithium source. In order to obtain the sols with different viscosities, the solution was evaporated at 60 °C for different periods. So the symbol from (a) to (e) in Fig. 2 represents the sols obtained with different evaporating times and thus the different viscosities. As seen, the viscosity of the sol almost kept constant as the shear rate increased, indicating the stability of the sol. Gel-spheres with homogeneous component could therefore be fabricated from the stable sol. Fig. 3 shows the morphology of the gel-spheres fabricated from the sols with different viscosities. It was found that if the viscosity was too high, such as 9600 mPa s, the sol was difficult to leave from the nozzle and the obtained gel-spheres usually possessed long tails, as shown in Fig. 3(c). On the contrary, if the viscosity was too low, such as 1600 mPa s, the sol could not keep the spherical shape while it was dropped into the acetone and the obtained gel-spheres usually looked like compressed spheres, as shown in Fig. 3(a). It was suggested that the viscosity of the sol should be adjusted to the range of 3400–8000 mPa s in order to obtain gel-spheres with favorable sphericity (as shown in Fig. 3(b)).

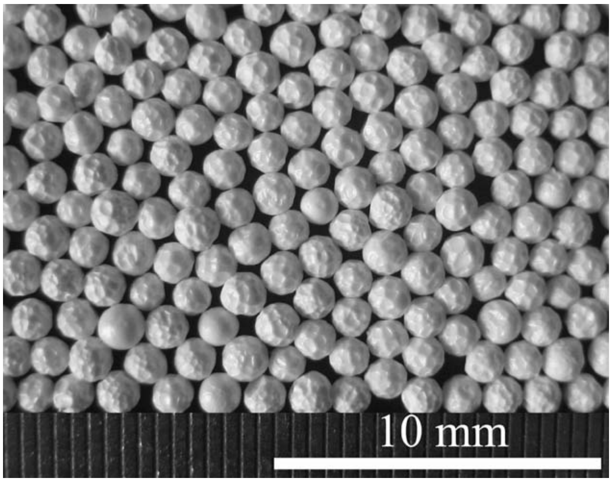

Fig. 1. The morphology of the sintered Li_2TiO_3 pebbles fabricated by the optimized sol–gel method.

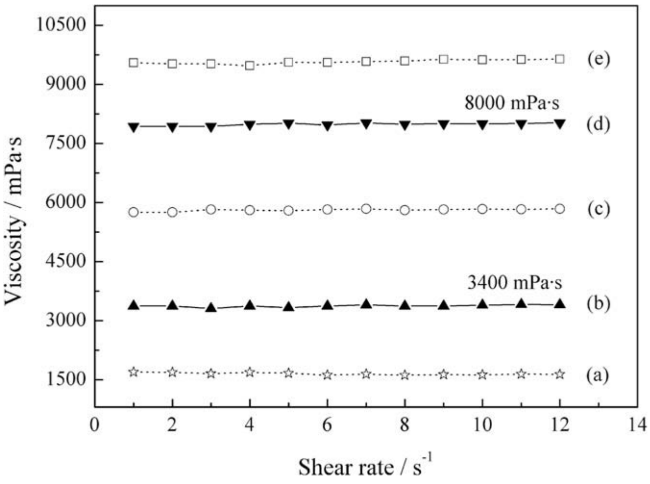

Fig. 2. Variation of the viscosity of the sol as a function of the shear rate.

3.3. Thermal treatment of the gel-spheres and phase evolution

Thermal treatment of the gel-spheres was conducted by thermal analyzer. Fig. 4 presents the typical TG/DSC profiles of the gel-spheres fabricated at pH 8.5 with LiOH as the lithium source. As observed, two obvious exothermic peaks at 385 and 520 °C were found on DSC curve, which might be ascribed to the decomposition of metal citrate and the formation of Li_2TiO_3, respectively. The decomposition of metal citrate also gave rise to the two weight losses in TG curve, because there was no other organism except citrate in the gel system. The total weight loss was about 70% in TG curve, that's to say, the solid content in the gel-spheres was about 30%. Compared to the thermal treatment results obtained by using $LiNO_3$ as the lithium source, the solid content was comparable for the two gel-precursors [11]. However, the thermal events were fewer in this work, indicating a simpler decomposition mechanism, which might be helpful to the densification of the gel-spheres during sintering process.

Phase evolution of the gel-spheres during the thermal treatment was also investigated. In Fig. 5, the XRD patterns of the gel-spheres sintered at different temperatures for 4 h are exhibited. As seen, the gel-spheres were carbonized when calcined at 265 °C, resulting in amorphous powder. Two broad peaks corresponding to the main diffraction lines of Li_2TiO_3 at (2 0 2) and (3 1 2) were found on the XRD patterns for the gel-spheres calcined at 385 or 520 °C, indicating the formation of amorphous or ultrafine Li_2TiO_3 powders. The two diffraction peaks became sharper while the sintering temperature increased to 600 °C. Further

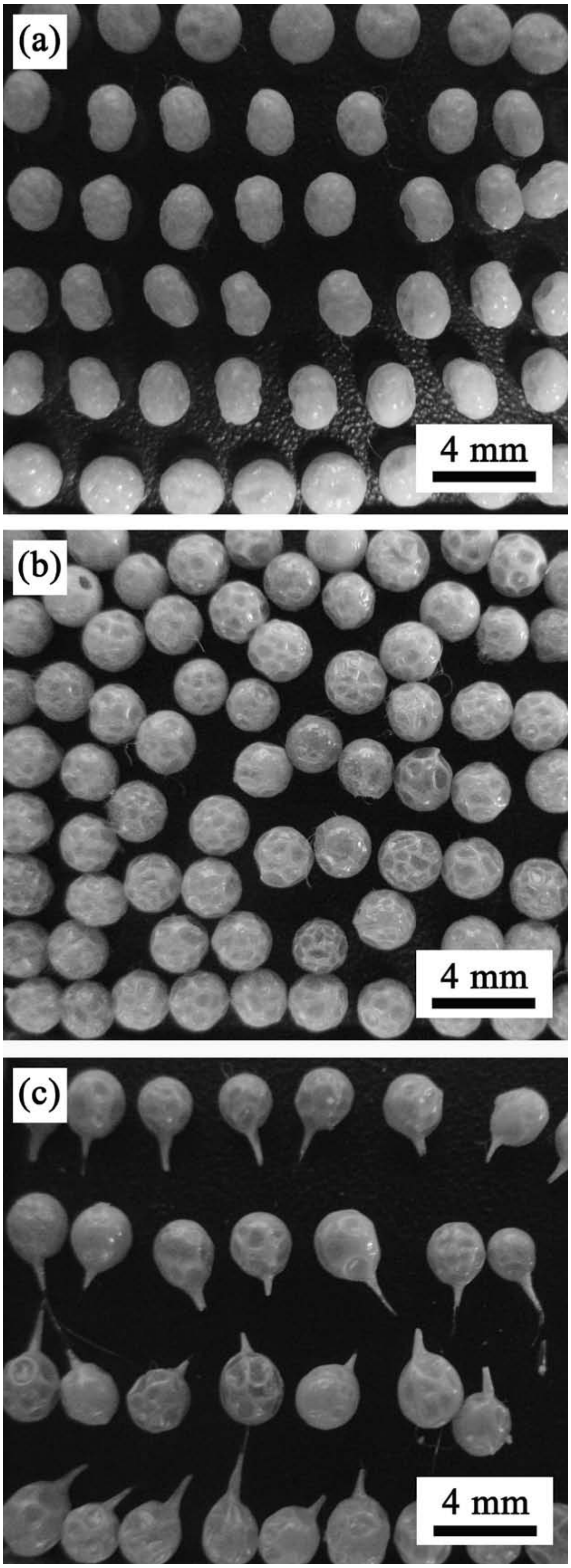

Fig. 3. Gel-spheres obtained at different viscosity: (a) 1600 mPa s, (b) 5800 mPa s and (c) 9600 mPa s.

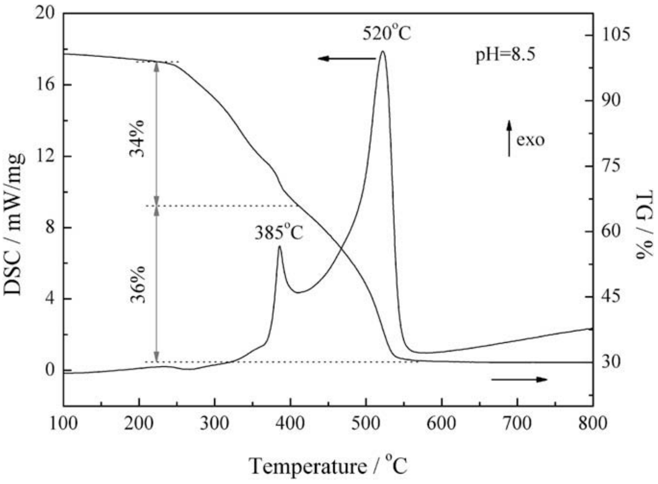

Fig. 4. The TG/DSC profiles of the gel-spheres during the thermal treatment.

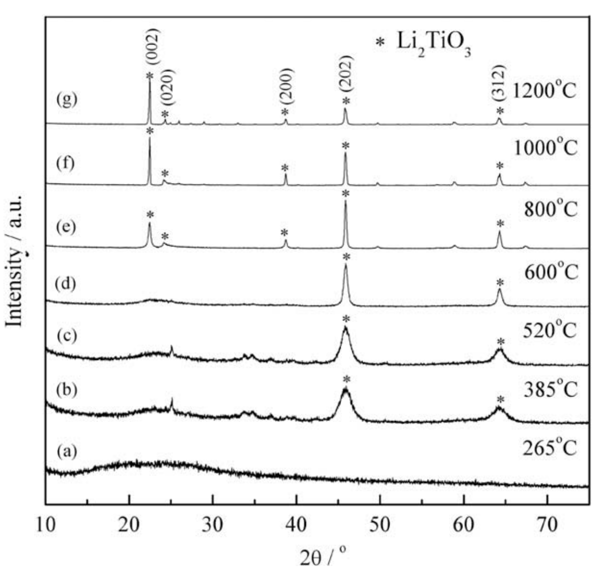

Fig. 5. XRD patterns of the gel-spheres sintered at different temperatures.

increase of the sintering temperature to 800, 1000 and 1200 °C did not result in any new diffraction peaks except the increase in the diffraction strength of Li_2TiO_3 phase. That is to say, Li_2TiO_3 ceramic spheres could be obtained by sintering the gel-spheres at 800–1200 °C without worrying about the formation of impurity phases. It was found that the intensity of peak (2 0 2) was higher than that of peak (0 0 2) at lower temperature, as shown in Fig. 5(d) and (e), however, it reversed at higher temperature, as shown in Fig. 5(f) and (g). The similar phenomenon was also observed previously [9].

3.4. Effect of the sintering temperature on the microstructure and density of Li_2TiO_3 pebbles

According to TG/DSC curves, the gel-spheres were calcined at 385 and 520 °C for 2 h, respectively, with a heating rate of 1 °C/min in order to remove the organism in the gel-spheres. Then, the calcined spheres were sintered at 950, 1000, 1100 and 1200 °C, respectively, for 4 h. The surface microstructure of the Li_2TiO_3 pebbles was shown in Fig. 6. As observed, the microstructure was significantly influenced by the sintering temperature. When sintered at 950 °C, two kinds of grains were seen. The majority of the grains were smaller than 1 μm and a few big ones were as large as about 5 μm. The grains became bigger and more homogeneous

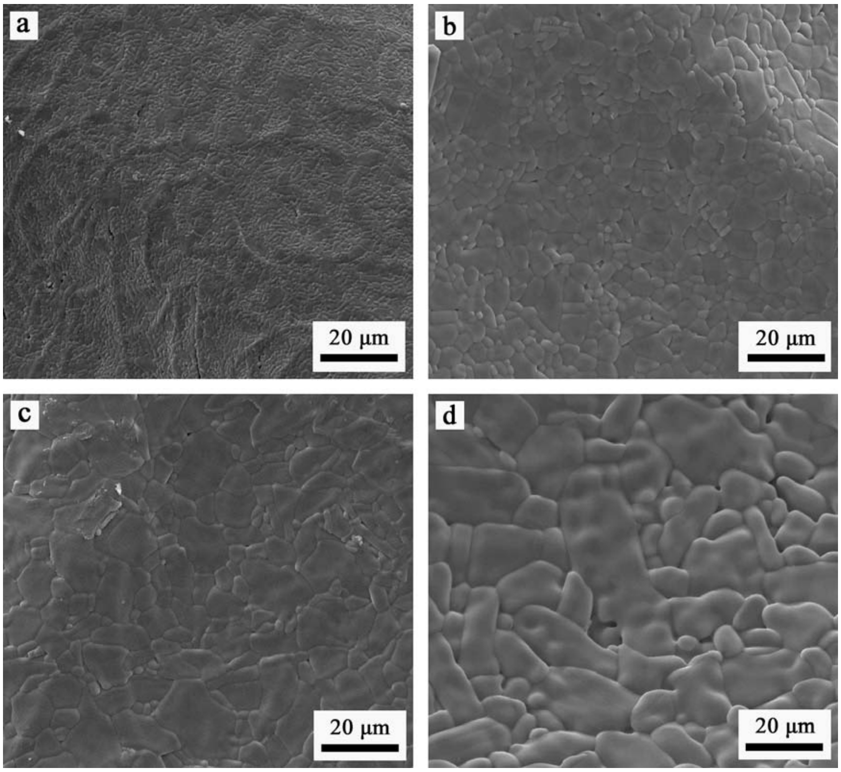

Fig. 6. SEM images of the Li_2TiO_3 pebbles sintered at (a) 950 °C, (b) 1000 °C, (c) 1100 °C and (d) 1200 °C.

and the average grain size was about 5 μm when sintered at 1000 °C. Most grains grew to 10 μm when the sintering temperature increased to 1100 °C and the surface of the pebbles seemed to be denser. Further increasing the sintering temperature to 1200 °C, the grains overgrew with size larger than 20 μm. Compared to the pebbles obtained by using $LiNO_3$ as the lithium source [11], the pebbles in this work contained much smaller pores and displayed much denser structure.

The sintered density of the Li_2TiO_3 pebbles was measured at room temperature. The relationship between the relative density and the sintering temperature is demonstrated in Fig. 7. As seen in Fig. 7, the relative density of the pebbles increased sharply with the increase in the temperature and reached as high as 83%T.D. at the temperature as low as 1000 °C. Further increase in the sintering temperature resulted in only slight change in the sintered density. The highest density about 85%T.D. was achieved at 1100 °C. It was indicated that by using LiOH instead of $LiNO_3$ as the lithium source, a favorable density (83%T.D.) was obtained though the Li_2TiO_3 pebbles were sintered at a relatively lower temperature (1000 °C) and shorter sintering time (4 h) [11].

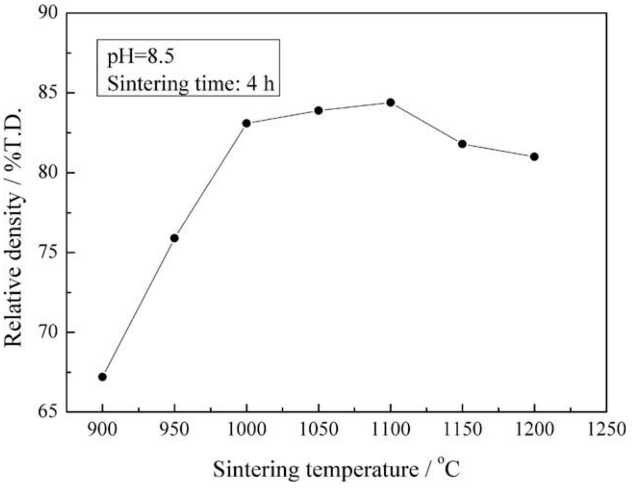

Fig. 7. The plot of the density of the pebbles versus sintering temperature.

3.5. Effect of the pH value on microstructure of Li_2TiO_3 pebbles

The influence of pH value on the microstructure of the pebbles was also investigated. Li_2TiO_3 pebbles were fabricated at pH values of 6.5, 8.5, 12.5, respectively, and then sintered at 1100 °C for 4 h. The pH value of the solution was related to the molar ratio of citric acid to LiOH. It was found that the pH value of the solution reached 6.5, 8.5 and 12.5 at the molar ratio of citric acid to LiOH of 10:24, 8:24 and 7:24, respectively. The higher the molar ratio of citric acid to LiOH, the lower the pH value of the solution. The microstructure for the fracture of the pebbles is exhibited in Fig. 8. It seemed that the microstructure was to some extent different from the surface of the pebbles. By comparing Fig. 6(c) with Fig. 8(a), it was seen that the interior of the pebbles was not as dense as the natural surface, some small pores and microcracks were found in the interior of the pebbles, which explained why the sintered density of the pebbles was not as high as expected from the surface microstructure. As observed in Fig. 8, the interior of the pebbles fabricated at pH 8.5 and 12.5 was almost equally dense (Fig. 8(a) and (b)). Though the pH value was much different, the amount of citric acid used to adjust the pH value of the LiOH solution was comparable because there was a sudden change for the pH value around the stoichiometric point (pH 8.5), which explained the reason of the similar fracture microstructures. However, the pebbles fabricated at pH 6.5 were very porous, as shown in Fig. 8(c). Pores larger than 20 μm were found in the interior of the sintered pebbles with density less than 30%T.D. Much more citric acid was necessary to adjust the pH value of the solution to 6.5 because of the weak acidity of citric acid, and the amount of gases generated during

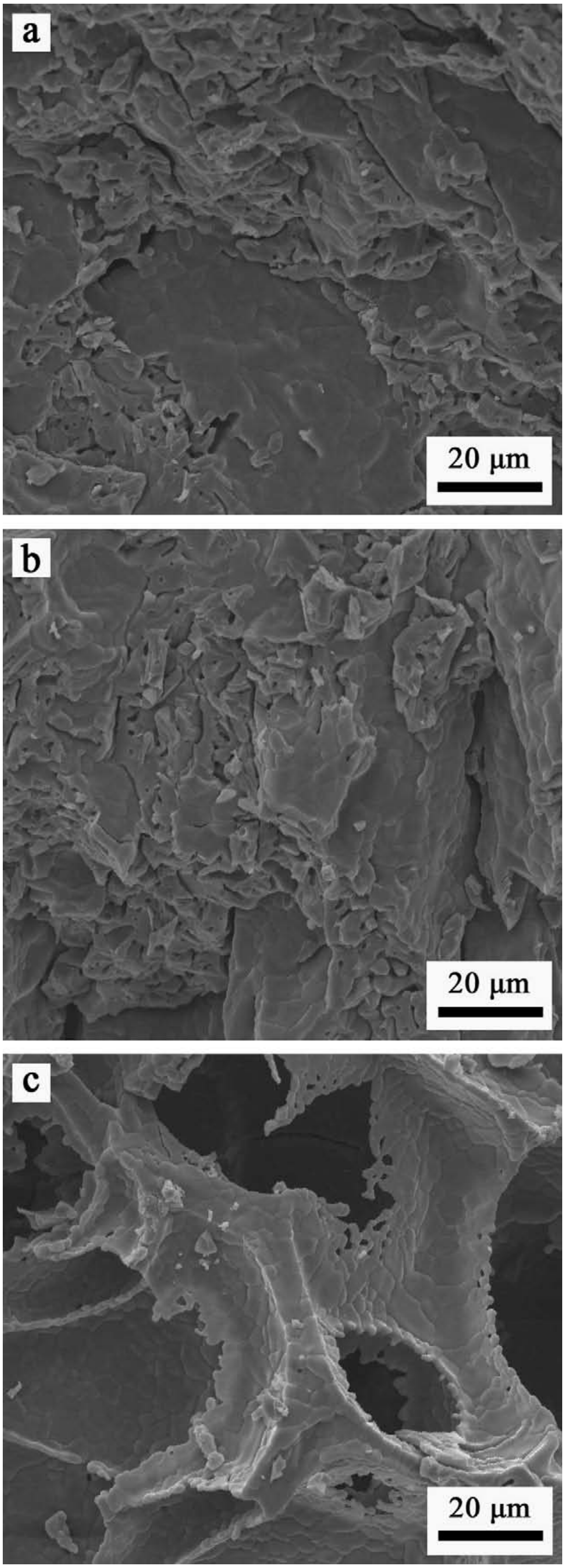

Fig. 8. The fracture microstructure of the Li_2TiO_3 pebbles fabricated at pH (a) 8.5, (b) 12.5 and (c) 6.5.

the sintering process increased greatly, which should be responsible for the porous structure.

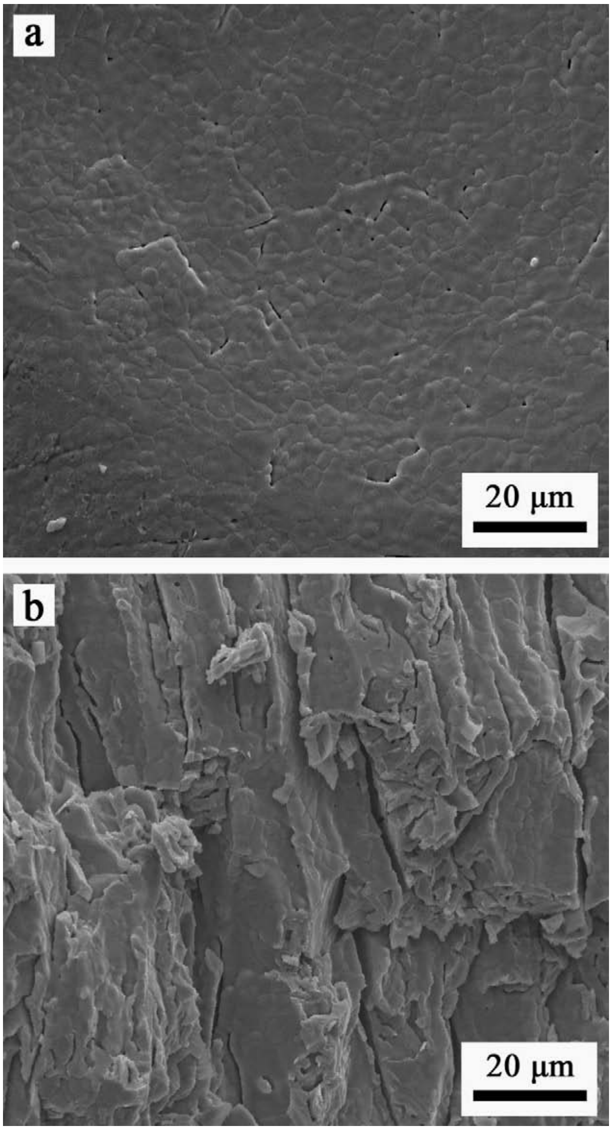

Fig. 9. The (a) surface and (b) fracture microstructure of the Li_2TiO_3 pebbles obtained by using CH_3COOLi as the lithium source.

3.6. Effect of the variety of lithium source on microstructure of Li_2TiO_3 pebbles

CH_3COOLi was also chosen as the lithium source in order to further investigate the effect of lithium source on the microstructure of Li_2TiO_3 pebbles. Fig. 9 presents the microstructure of the Li_2TiO_3 pebbles prepared by using CH_3COOLi as the lithium source. As shown in Fig. 9, the average particle size was about 5 μm, which was smaller than that of the pebbles sintered at the same sintering conditions by using LiOH as the lithium source (Fig. 6(c)). Some small pores and microcracks were seen both on the surface and in the interior of the pebbles. The density of the pebbles sintered at 1100 °C for 4 h was about 80%T.D., which was lower than that of the pebbles obtained by using LiOH as the lithium source, but much higher than that of the pebbles obtained by using $LiNO_3$ as the lithium source at the same sintering conditions.

4. Conclusions

Li_2TiO_3 pebbles with diameter of about 1.24 mm were fabricated by using dissolvable lithium salts and titanium salt as the raw materials. The shape of the obtained pebbles was nearly spherical but further work need to be done to smooth the surface of the pebbles. The following conclusions could be confirmed:

(1) The viscosity of the sol had a significant influence on the sphericity of the gel-spheres and thus the sintered pebbles. Gel-spheres with adequate sphericity could be fabricated from the sol with the viscosity in the range of 3400–8000 mPa s.
(2) It was the most advantageous to the improvement of the sintered density of Li_2TiO_3 pebbles by using LiOH as the lithium source instead of $LiNO_3$ and CH_3COOLi.
(3) The microstructure of the pebbles was susceptible to the sintering temperature. It was suggested that the pebbles should be sintered at 1000–1100 °C in order to obtained favorable microstructure and relatively high density (83–85%T.D.).
(4) It was beneficial to the densification of the ceramic pebbles to adjust the pH value of the solution in the range of 8.5–12.5.

References

[1] J.G. van der Laan, H. Kawamura, N. Roux, D. Yamaki, J. Nucl. Mater. 283–287 (2000) 99.
[2] A. Ying, M. Akiba, L.V. Boccaccini, S. Casadio, G. Dell'Orco, M. Enoeda, et al., J. Nucl. Mater. 367–370 (2007) 1281.
[3] N. Roux, S. Tanaka, C. Johnson, R. Verrall, Fusion Eng. Des. 41 (1998) 31.
[4] C.E. Johnson, K. Noda, N. Roux, J. Nucl. Mater. 258–263 (1998) 140.
[5] J.D. Lulewicz, N. Roux, Fusion Eng. Des. 39–40 (1998) 745.
[6] J.G. van der Laan, R.P. Muis, J. Nucl. Mater. 271–272 (1999) 401.
[7] K. Tsuchiya, H. Kawamura, J. Nucl. Mater. 283–287 (2000) 1380.
[8] K. Tsuchiya, H. Kawamura, T. Takayama, S. Kato, J. Nucl. Mater. 345 (2005) 239.
[9] K. Tsuchiya, H. Kawamura, S. Casadio, C. Alvani, Fusion Eng. Des. 75–79 (2005) 877.
[10] Xiangwei Wu, Zhaoyin Wen, Xiaoxiong Xu, Zhonghua Gu, Xiaohe Xu, J. Nucl. Mater. 373 (2008) 206.
[11] Xiangwei Wu, Zhaoyin Wen, Jinduo Han, Xiaoxiong Xu, Bin Lin, Fusion Eng. Des. 83 (2008) 112.
[12] J.D. Lulewicz, N. Roux, J. Nucl. Mater. 307–311 (2002) 803.