ELSEVIER

Available online at www.sciencedirect.com

ScienceDirect

Journal of Nuclear Materials 373 (2008) 206–211

journal of nuclear materials

www.elsevier.com/locate/jnucmat

Optimization of a wet chemistry method for fabrication of Li_2TiO_3 pebbles

Xiangwei Wu, Zhaoyin Wen *, Xiaoxiong Xu, Zhonghua Gu, Xiaohe Xu

Shanghai Institute of Ceramics, Chinese Academy of Sciences, Graduate School, 1295 Ding Xi Road, Shanghai 200050, PR China

Received 21 November 2006; accepted 24 May 2007

Abstract

Li_2TiO_3 is one of the most promising candidates for solid breeder materials. Li_2TiO_3 pebbles with about 1.20 mm in diameter and 91%T.D. were successfully prepared by an optimized wet chemistry method using citric acid as chelating agent. Thermal analysis, phase analysis and morphological observations were carried out systematically. The experimental results showed that the amount of the chelating agent influenced obviously the sphericity of the pebbles. The prepared pebbles displayed a homogeneous and temperature sensitive microstructure with an average grain size less than 3 μm while sintered at 1050 °C for 6 h.

1. Introduction

Lithium-based ceramics, such as Li_2O,Li_2ZrO_3, Li_2TiO_3, Li_4SiO_4 etc. were recognized as candidates for tritium breeding materials in fusion reactors [1,2]. Among them, lithium titanate (Li_2TiO_3) is considered to be one of the most promising candidates because of its reasonable lithium atom density, low activation, high chemical stability, good compatibility with structural materials and excellent tritium release characteristics at low temperatures [3–6].

The pebble configuration has been adopted as the preferred option for tritium breeders in the assembly of blankets with complex geometry and with regard to thermal stress and irradiation cracking [7]. Many techniques can be used to fabricate lithium titanate pebbles, e.g. solid-state reaction-based techniques involving the extrusion–spheronization–sintering process, agglomeration–sintering process and rotating granulation and wet processes such as the sol–gel method, soft chemistry method etc [8–11].

Usually, high amounts of binders must be used in the process of pebble fabrication by solid-state reaction techniques. The combustion of the binders during sintering of the pebbles would generate a lot of gas which prohibited the densification of the pebbles and led to unsatisfied density. The wet process such as the sol–gel method, soft chemistry method etc. received particular attention since no binder was used for the process and high density was therefore easily realized. Moreover, it is convenient to realize mass production by such methods, and it is advantageous from the viewpoint of reprocessing lithium-bearing solutions.

Tsuchiya et al. have studied the preparation of Li_2TiO_3 pebbles by the direct-wet process with H_2O_2 as the solvent. Although gel spheres with favorable sphericity could be fabricated when the mixed solution of 30% H_2O_2 and citric acid ($C_6H_8O_7$) was used as the solvent, it is difficult to produce dense pebbles by the post-sintering of the gel spheres [12]. In this paper, by optimizing the process parameters, Li_2TiO_3 pebbles with density as high as 91%T.D. were produced by the wet chemistry method based on 30% H_2O_2 + citric acid ($C_6H_8O_7$) solvent, influence of citric acid ratio of the solvent, handling temperature etc. on the quality of the pebbles was systematically investigated.

---

* 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 © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.jnucmat.2007.05.045

2. Experiments

2.1. Preparation of the Li_2TiO_3 powder

Precursor Li_2TiO_3 powder was synthesized by the solid state reaction technique at 700 °C for four hours based on the following chemical reaction:

$$Li_2CO_3 + TiO_2 \rightarrow Li_2TiO_3 + CO_2 \uparrow$$

Appropriate amounts of Li_2CO_3 (A.R.) and TiO_2 (A.R.) powders corresponding to the Li/Ti atomic ratio of 2 in the final ceramic products were blended by planetary ball milling for 4 h with ethyl alcohol as the milling medium. Li_2TiO_3 powders were formed by calcining the dried precursors at 700 °C for 4 h in air atmosphere.

2.2. Fabrication of Li_2TiO_3 pebbles

Fig. 1 shows the flow chart of the process for pebble preparation. A 30 wt% aqueous solution of H_2O_2 was selected as the solvent for dissolving Li_2TiO_3, and citric acid ($C_6H_8O_7$) was used as the chelating agent. The solution was heated at 60 °C in an oil bath. The reaction was highly exothermic with a lot of foam appeared. During the heating treatment, the color of the solution firstly changed to orange-red, the heating lasted until the Li_2TiO_3 content of the solution reached 25 wt%. Then the concentrated liquid was dropped into the gelation bath with acetone as the gelating agent to form gel spheres. Subsequent aging was processed at ambient temperature for sufficient time. Then the gel spheres were dried at 50 °C in air. Finally, the loose pebbles were sintered at 1050 °C for 6 h in air atmosphere.

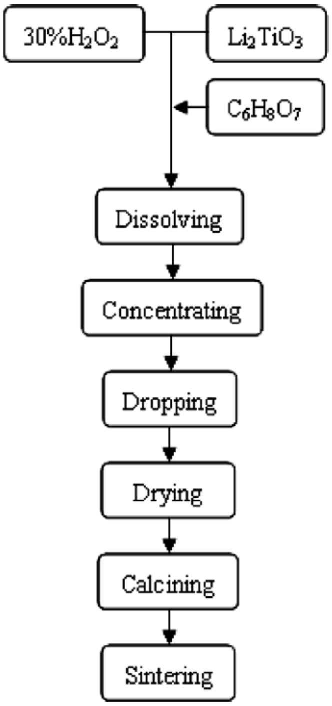

Fig. 1. Flow chart of the optimized wet chemistry method.

2.3. Characterizations

Thermal analysis of the gel spheres was performed by thermogravimetry and differential analysis (NETZSCH, STA 409 PC) in air atmospheres at a heating rate of 10 °C /min the temperature range between room temperature and 800 °C. The density of the Li_2TiO_3 pebbles was measured by Archimedes' principle using ethyl alcohol as the medium. The crystalline phases were identified by X-ray diffraction analysis (Rigaku RAD-C, 12KW) at room temperature using Cu Kα radiation, and the surface microstructure of the sintered pebbles was observed by scanning electron microscopy (EPMA-8705QH_2).

3. Results and discussion

3.1. Pebbles characteristics

Fig. 2 shows the morphology of a batch of Li_2TiO_3 pebble. As seen, the shape of Li_2TiO_3 pebbles was nearly spherical with the sphericity, denoted as the ratio of the maximum diameter/minimum diameter [13], of about 1.05. The diameter of the pebbles was measured by sieve classification method and distributed in the range of 1.09–1.32 mm. The average diameter of the pebbles was about 1.20 ± 0.03 mm. The density of the pebbles was measured at room temperature. A small batch of pebbles (about 50 pebbles) was tested together with the measurement of the density. When the citric acid/Li_2TiO_3 molar ratio was fixed at 1, the pebbles sintered at 1050 °C for 6 h reached an average density as high as 91%T.D.

3.2. The thermal treatment process

The sample with 18.8 mg in weight was used in the thermal treatment. Fig. 3 shows the TG/DTA profile of the gel precursor, four peaks at 125 °C, 180 °C, 370 °C and 495 °C, respectively, were observed on the DTA curve. The endothermic peak at 125 °C was ascribed to the evaporation of absorbing H_2O, the corresponding weight loss about 12% was found. Decomposition of H_2O_2 gave rise

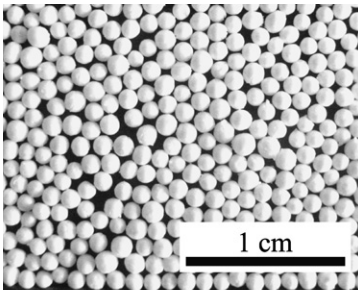

Fig. 2. The photograph of Li_2TiO_3 pebbles.

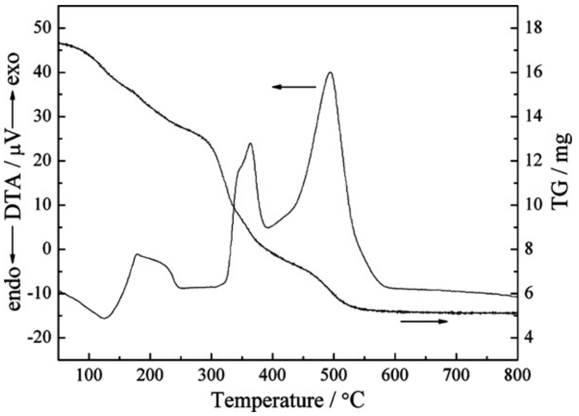

Fig. 3. TG/DTA curves of gel spheres.

to the exothermic peak at 180 °C with a weight loss of about 13%. Significant weight loss as high as about 30% took place at 300–450 °C, which might be attributed to the release of CO and CO_2. The strongest exothermic peak appeared at 495 °C, might be ascribed to the formation of Li_2TiO_3phase. No further thermal effect and weight change were found on the TG/DTA curves above 550 °C. Based on the thermal analysis results, the calcination of gel spheres was conducted in four steps, i.e., at 125 °C, 180 °C, 370 °C and 495 °C, respectively, for 5 h at each step.

3.3. Phase evolution

In order to avoid the production of $LiTiO_2$ phase, all the pebbles were sintered in air atmosphere, since Ti can be reduced from the 4-valence state to the 3-valence state at low oxygen partial pressures [15]. XRD data shown in Fig. 4 indicates the evolution of phases during the fabrication process. The data shows that the orange-red gel spheres obtained after drying at 50 °C consist of Li–Ti–peroxo complexes and similar observations have been made by Tsuchiya et al. [11]. No peaks were presented on the XRD pattern (Fig. 4(b)) of the gel spheres calcined at 200 °C for 4 h, indicating that the gel spheres became completely amorphous. During this period, the color of the gel spheres changed gradually from orange-red to brown. A broad peak at 2θ of 43.6 degree was observed as shown in Fig. 4(c) while the calcining temperature was further increased to 370 °C, but its intensity was very weak. The color of the spheres became black while sintered at 370 °C. After calcination at 495 °C for 4 h, the color of the spheres changed to white and the formation of the Li_2TiO_3 phase was observed on XRD pattern. The broad peaks corresponding to the main diffraction lines of Li_2TiO_3 demonstrated the ultra-fine or amorphous feature of the Li_2TiO_3 phase (Fig. 4(d)). Sharp peaks corresponding to the pure Li_2TiO_3 phase was obtained from the spheres sintered at both 750 °C and 1050 °C. The obtained Li_2TiO_3 phase was monoclinic, and Li/Ti molar ratio was 2. High purity silicon powders were used as an internal standard to determine the lattice parameters. The results were as follows: $a = 508.3$ pm, $b = 872.2$ pm, $c = 976.0$ pm and $\beta = 100.8°$. These results were in consistent with the values reported by Kleykamp [15]. Compared to the precursor powder prepared by solid state reaction, a major difference in the relative strength of the peaks of (0 0 2) to $(\bar{1}\,3\,3)$ was found. It is seen from the figure that with increasing in temperature, the relative strength of the (0 0 2) peak became stronger and stronger compared to that of the peak $(\bar{1}\,3\,3)$, indicating that the effect of high temperature was beneficial to the growth of the crystal plane (0 0 2). Obviously, grain growth at high temperature made the half-width of the peaks narrower.

3.4. Effect of citric acid

3.4.1. Effect of citric acid on the sphericity

The amount of the chelating agent, citric acid, was important to the performance of the gel and thus the sphericity of the pebbles. The influence of the molar ratio of citric acid/Li_2TiO_3 on the sphericity of the prepared

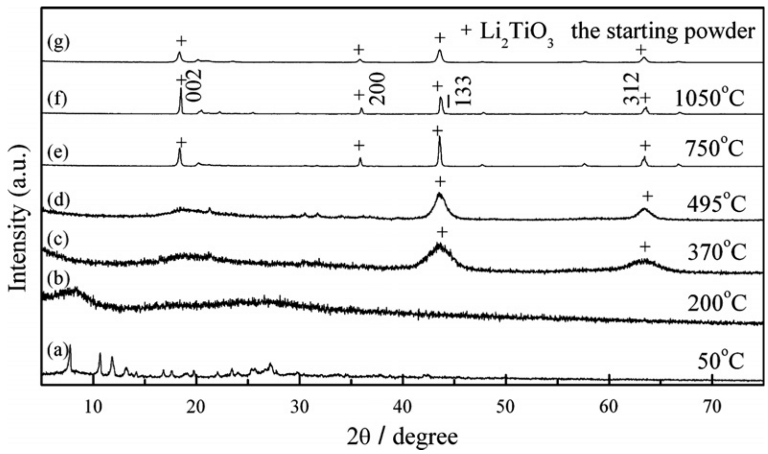

Fig. 4. XRD patterns of the gel spheres (a) dried at 50 °C, (b) calcined at 200 °C, (c) calcined at 370 °C, (d) calcined at 495 °C, (e) sintered at 750 °C, (f) sintered at 1050 °C and (g) the starting powder prepared by solid state reaction.

pebbles was investigated. The sphericity of a pebble is denoted as the ratio of its maximum diameter value to its minimum one. The sphericity of a perfect sphere then is 1. A pebble deviates from the perfect sphere more while the value of sphericity is farther away from 1.

Fig. 5 shows typical morphology of pebbles prepared at different citric acid/Li_2TiO_3 ratios. As seen, the ratio remarkably affected the morphology or the sphericity of the pebbles.

Fig. 6 illustrates the relationship between the sphericity and the citric acid/Li_2TiO_3 molar ratio. It was seen that the sphericity was significantly influenced by the molar ratio, moreover, a best sphericity about 1.05 was obtained at the molar ratio of 1.0. It seemed that lower molar ratio was beneficial to the sphericity of the pebbles, the molar ratio higher than 1.0 resulted in great deviation from perfect spheres for the pebbles. What is more, the error for

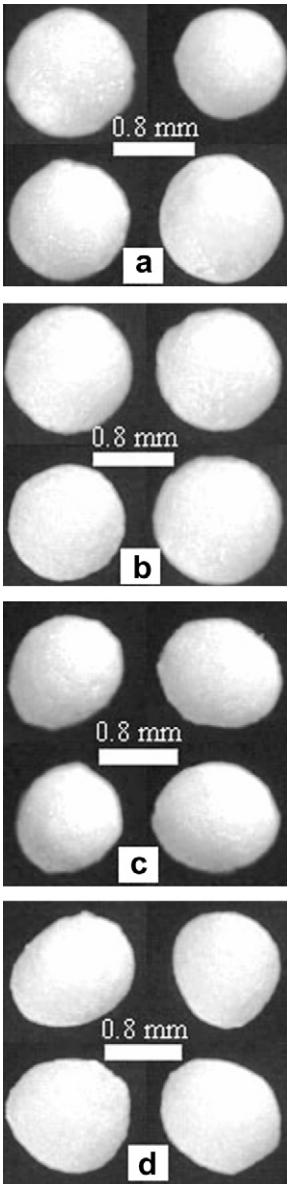

Fig. 5. The morphology of the pebbles obtained at different molar ratios of citric acid/Li_2TiO_3, (a) 0.75:1, (b) 1:1, (c) 1.25:1 and (d) 1.5:1.

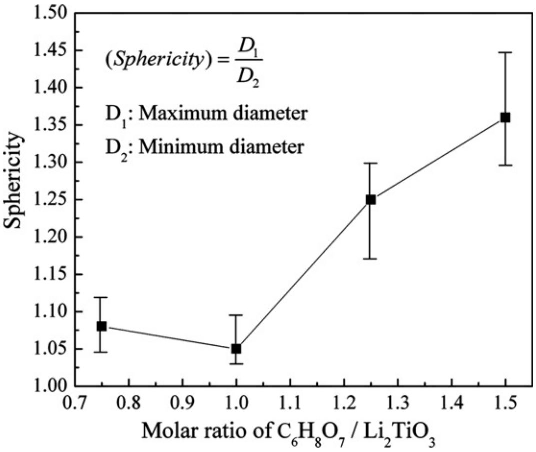

Fig. 6. Relationship between sphericity of the pebble and the citric acid/Li_2TiO_3 molar ratio.

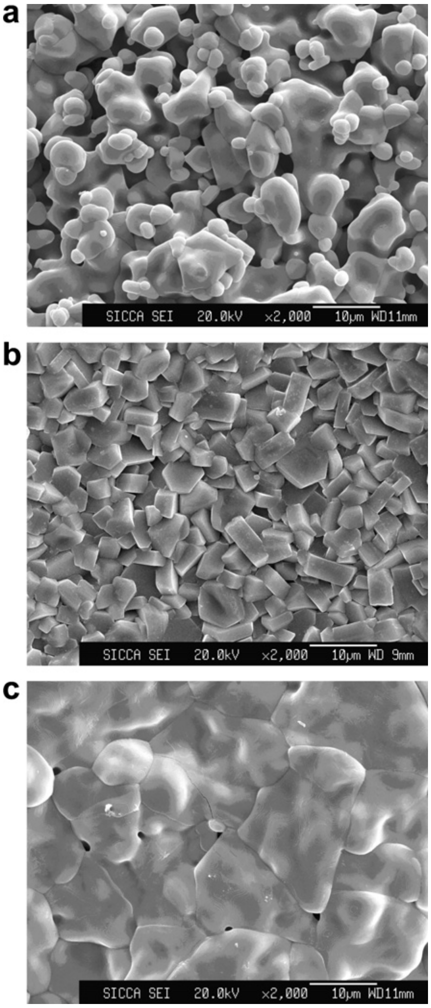

Fig. 7. SEM micrographs of the surface of Li_2TiO_3 pebbles prepared at (a) $C_6H_8O_7/Li_2TiO_3 = 0.75$, (b) $C_6H_8O_7/Li_2TiO_3 = 1$, and (c) $C_6H_8O_7/Li_2TiO_3 = 1.5$.

the sphericity was the narrowest when the citric acid/ Li_2TiO_3 molar ratio was 1.0. It was found that the optimum molar ratio coincided with the stoichiometry of the following reaction for the gel preparation system [14]:

$$2Li_2TiO_3(s) + 2H_2O_2(aq) + H_2O(l) \rightarrow Li_4Ti_2O_5(OH)_6(aq) \quad (1)$$

$$Li_4Ti_2O_5(OH)_6(aq) + 2C_6H_8O_7 \cdot H_2O(aq) \rightarrow Li_4[Ti_2O_5(C_6H_5O_7)_2](aq) + 8H_2O(l) \quad (2)$$

3.4.2. Effect of citric acid on the microstructure of the pebbles

Fig. 7 shows the microstructure of Li_2TiO_3 pebbles sintered at 1050 °C for 6 h. Fig. 7(a–c) correspond to the pebbles obtained at the citric acid/ Li_2TiO_3 molar ratio of 0.75, 1 and 1.25, respectively. As seen, the amount of citric acid had a great influence on the microstructure of the pebbles. When the amount of citric acid was insufficient, the pebbles were very porous as shown in Fig. 7(a). Some pores connected with each other and micro-cracks were easily formed. Many pebbles cracked during the fabrication process. If the amount of citric acid was excessive, e.g., $C_6H_8O_7/Li_2TiO_3 = 1.5$, overgrowth of grains was obvious with grain sizes larger than 10 μm and grain boundaries became illegible. Furthermore, pores became less and smaller as indicated in Fig. 7(c). It was noted that the stoichiometric amount of citric acid was favorable to obtain the ceramic pebbles with good microstructure. As seen in Fig. 7(b), the grains were well grown with sizes in the range of 2–3 μm and relatively narrow distribution. Only few pores with sizes less than 2 μm were observed from the surface of the pebbles, which proved the high density above 91%T.D.

3.5. Effect of sintering temperature on microstructure

The effect of sintering temperature on the microstructure of Li_2TiO_3 pebbles was examined. All the pebbles were prepared with $C_6H_8O_7/Li_2TiO_3 = 1$ (in molar). Fig. 8(a–c) and Fig. 7(b) show the surface microstructure of the Li_2TiO_3 pebbles sintered at 750 °C, 950 °C, 1150 °C, and 1050 °C, respectively, for 6 h. As observed, the grains did not grow well when the pebbles were sintered at the temperature as low as 750 °C, resulting in a lot of pores on the surface of the pebbles. Therefore, low temperature was disadvantageous to the densification of the pebbles. When the sintering temperature increased to 950 °C, the morphology of the gains became more favorable. Good microstructure was obtained in the ceramic pebbles sintered at 1050 °C. The grains grew well with sizes in the range of 2–3 μm and narrow distribution. Few pores were observed. Further increase of the sintering temperature to 1150 °C led to the grains grown to over 20 μm and the grains displayed melting feature, which was adverse to the packing process between grains.

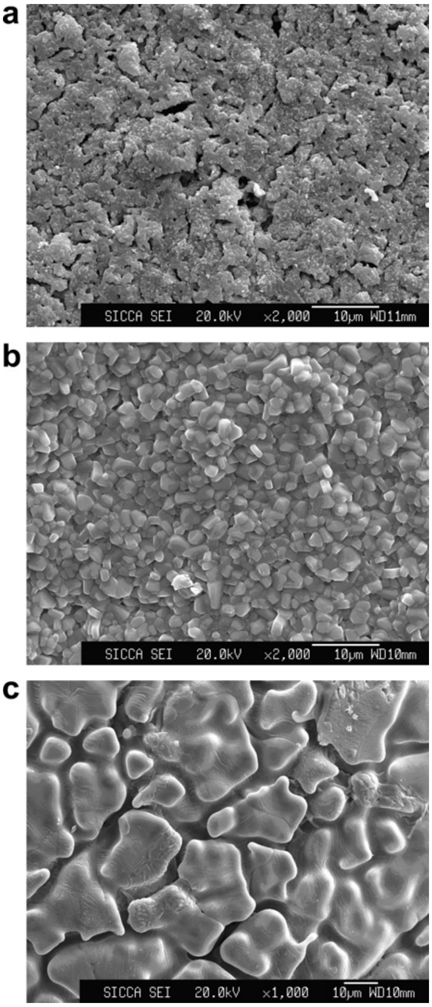

Fig. 8. SEM micrographs of the surface of Li_2TiO_3 pebbles sintered at (a) 750 °C, (b) 950 °C and (c) 1150 °C.

4. Conclusions

The fabrication process of Li_2TiO_3 pebbles was performed by an optimized wet chemistry method and the following conclusions can be confirmed:

(1) Li_2TiO_3 pebbles with diameter of about 1.20 mm, density about 91%T.D. and grain size of 2–3 μm can be fabricated by an optimized wet chemistry method with $30\%H_2O_2$ + citric acid ($C_6H_8O_7$) as solution.
(2) The amount of citric acid was influential to the sphericity of the Li_2TiO_3 pebbles.
(3) The microstructure of the Li_2TiO_3 pebbles was sensitive to the sintering temperature.

References

[1] N. Roux, G. Hollenberg, C. Johnson, K. Noda, R. Verrall, Fusion Eng. Des. 27 (1995) 154.

[2] C.E. Johnson, K.R. Kummerer, E. Roth, J. Nucl. Mater. 155–157 (1988) 188.
[3] J.M. Miller, H.B. Hamilton, J.D. Sullivan, J. Nucl. Mater. 212–215 (1994) 877.
[4] N. Roux, J. Avon, A. Floreancing, J. Mougin, B. Rasneur, S. Ravel, J. Nucl. Mater. 233–237 (1996) 1431.
[5] H. Kleykamp, J. Nucl. Mater. 283–287 (2000) 1385.
[6] J.P. Kopasz, J.M. Miller, C.E. Johnson, J. Nucl. Mater. 212–215 (1994) 927.
[7] N. Roux, S. Tanaka, C. Johnson, R. Verrall, Fusion Eng. Des. 41 (1998) 31.
[8] J.D. Lulewicz, N. Roux, J. Nucl. Mater. 307–311 (2002) 803.
[9] J.D. Lulewicz, N. Roux, Fusion Eng. Des. 39&40 (1998) 745.
[10] J.G. van der Laan, R.P. Muis, J. Nucl. Mater. 271&272 (1999) 401.
[11] K. Tsuchiya, H. Kawamura, T. Takayama, S. Kato, J. Nucl. Mater. 345 (2005) 239.
[12] K. Tsuchiya, H. Kawamura, S. Casadio, C. Alvani, Fusion Eng. Des. 75–79 (2005) 877.
[13] K. Tsuchiya, H. Kawamura, J. Nucl. Mater. 283–287 (2000) 1380.
[14] C. Alvani, P.L. Carconi, S. Casadio, V. Contini, A. Dibartolomeo, F. Pierdominici, A. Deptula, S. Lagos, C.A. Nannetti, J. Nucl. Mater. 289 (2001) 303.
[15] H. Kleykamp, Fusion Eng. Des. 61&62 (2002) 361.