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Lithium orthosilicate as nuclear fusion breeder material: Optimization of the drip casting production technology

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ABSTRACT

The production of nuclear fusion energy, in the future DEMOnstration power plant (DEMO), is based on tritium self-sufficiency, achievable exploiting neutron-lithium reaction occurring in the breeding blanket modules. To fulfil the plant design conditions ceramic materials containing lithium are suggested. A lot of research efforts focused on the past years on the investigation and selection of the most suitable breeding material.

In this study, the lithium orthosilicate, in pebble form, produced at room temperature at the University of Pisa was investigated and characterized from a thermo-mechanical point of view. The pebbles were produced by a drip casting forming technique, starting from an aqueous suspension of a Li_4SiO_4 precursor obtained by hydrolytic sol–gel method, and dropping it into a calcium chloride/lithium acetate solution. A high temperature thermal treatment was applied to green pebbles to synthesize Li_4SiO_4 and densify the structure. Thermal analysis and static uniaxial compression tests, without radial constraints, were carried out on different types of pebbles produced varying the composition of the precursor suspension by means of cellulose fiber additions. Results show the influence of the cellulose content on morphological and physical properties of the obtained pebbles. Li_4SiO_4 pebbles with a density of 88 % and a crush load of about 30 N were obtained when the suspension was modified by adding 15 wt% of cellulose fibers to the sol–gel precursor powders.

1. Introduction

The production of nuclear energy through deuterium–tritium fusion technology is based on tritium generation by neutron irradiation of lithium in breeding blanket modules containing lithium-based materials. Currently, four types of breeding blanket concepts have been investigated in Europe and one of the most promising is the Helium Cooled Pebble Bed (HCPB) for future implementation in DEMOnstration power plant reactors (DEMO) [1]. Functional materials for the HCPB blanket modules are lithium ceramics in the form of pebble beds, which allow to have high resistance to thermal load, and the presence of interconnected spaces for helium pass-through for recovery of released tritium [2]. Several lithium ceramics have been proposed in the past years as breeding materials, such as lithium aluminate ($LiAlO_2$), lithium orthosilicate (Li_4SiO_4), lithium zirconate (Li_2ZrO_3) and lithium metatitanate (Li_2TiO_3) [3]. Among them, the main candidates for ceramic breeders are Li_4SiO_4 and Li_2TiO_3, thanks to their high density of lithium, good tritium release and low-activation energy [4]. More recently, the fabrication of bi-phasic pebbles has attracted great interest with the aim of enhancing the pebbles mechanical properties [5–13].

In this study, Li_4SiO_4 pebbles production has been investigated by means of drip casting technology [14–17] in order to obtain high compressive strength pebbles. Li_4SiO_4 pebbles were produced starting from a precursor synthesized employing the hydrolytic sol–gel method. The precursor suspension was modified by adding a thickening agent (cellulose fibers) and dropped into a calcium chloride/lithium acetate solution. Li_4SiO_4 pebbles were obtained after high-temperature thermal treatment. The effect of the cellulose fiber additions to the suspension on the pebbles properties was examined by carrying out thermal analysis, morphological characterization, and compression tests.

2. Experimental activities

2.1. Production of Li_4SiO_4 pebbles by drip casting methodology

The forming technique of drip casting for producing ceramic spheres at room temperature was used in this study to produce Li_4SiO_4 pebbles. A Li_4SiO_4 precursor with a cross-linked structure was synthesized by

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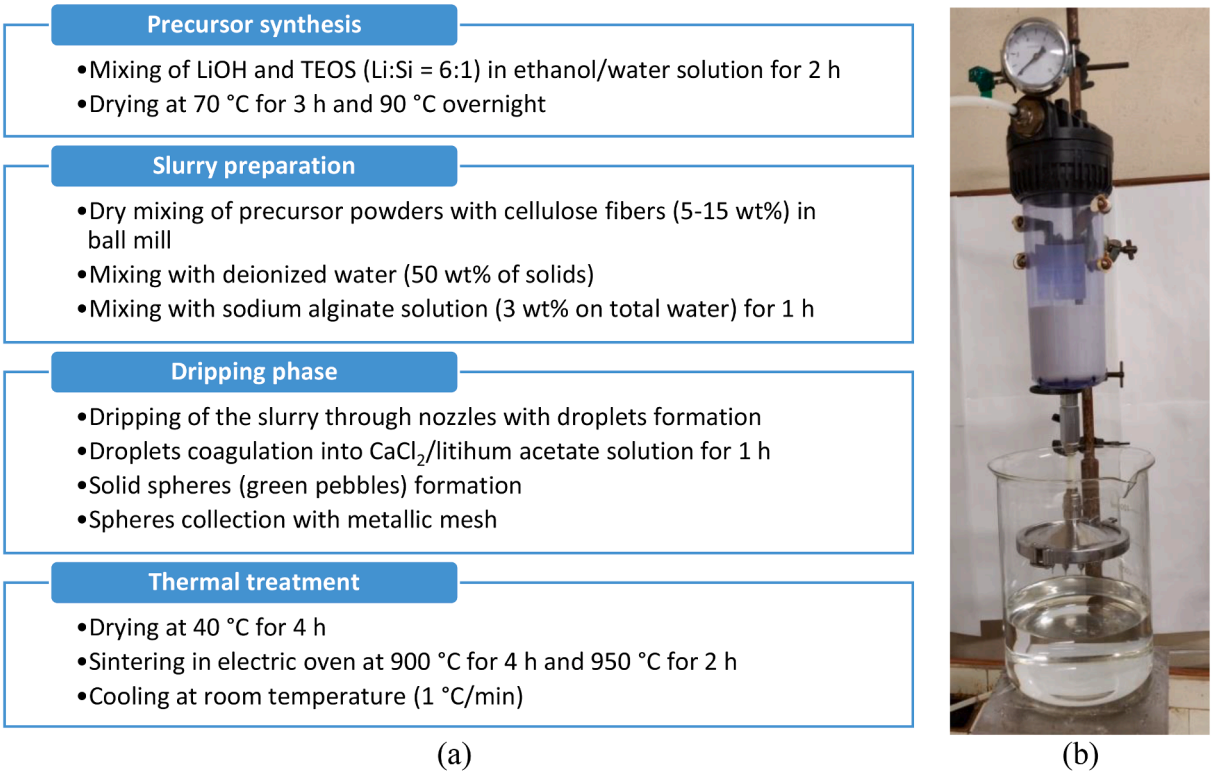

Fig. 1. The drip casting forming process developed at DICI: (a) main phases for pebbles fabrication, and (b) overview of the experimental test facility.

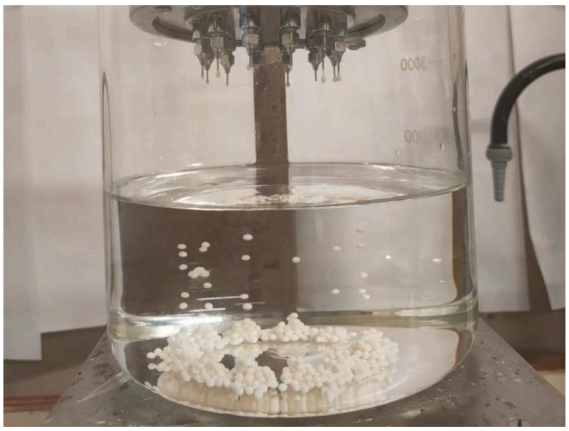

Fig. 2. Detail of the dripping phase: diffusion of the slurry through nozzles with droplets formation, and droplets gelation in the reacting solution.

hydrolytic sol–gel method, as described in our previous work [17], and used as starting material for the dripping process. The main phases of the drip casting method and an overview of the experimental device used are shown in Fig. 1. The experimental set-up is composed of a feeding tank for the ceramic suspension, a diffusion system (nozzle plate equipped with 12 nozzles, 0.8 mm internal diameter), and a reaction vessel, where gelation and hardening of the droplets occur. A detailed description of the test facility is reported in [14].

For the precursor synthesis, the starting materials were lithium hydroxide (LiOH) and tetraethyl orthosilicate ($Si(OCH_2CH_3)_4$, TEOS), both purchased from Sigma Aldrich. First, LiOH was dissolved in deionized water (11 wt% solution) and ethanol (C_2H_5OH). Then, TEOS was added to the mixture after 1 h (Li:Si = 6:1), and left under stirring at room temperature for 2 h, where hydrolysis and condensation reactions took place to form a cross-linked compound (called gel). Finally, the mixture was dried at 70 °C for about 3 h, and then at 90 °C overnight.

The resulting sol–gel powders were dry mixed in a rapid mill with cellulose fibers (Arbocel BE 600/30, average fiber length 30 μm, J. Rettenmaier & Söhne), then dispersed in deionized water (50 wt% total solids content), and a sodium alginate solution was added (3 wt% on total water). The obtained slurry was stirred for 60 min, then it was forced to pass through the nozzle plate and dropped into a reacting solution, containing calcium chloride ($CaCl_2$) aqueous solution (5 wt%) saturated with lithium acetate di-hydrate ($CH_3COOLi{\cdot}2H_2O$, powder) (29 wt%) (Fig. 2). The droplets coagulated into solid spheres thanks to the formation of cross-links among the alginate polymeric chains [14]. After 1 h, the obtained spheres (green pebbles) were collected, dried at 40 °C for 4 h, and sintered in air (first step: 900 °C for 4 h, second step: 950 °C for 2 h; heating rate: 1 °C/min). Sintering of green pebbles allows to decompose alginate network and cellulose fibers, synthesize Li_4SiO_4 from the sol–gel precursor, and shrink and densify the pebbles structure.

Three different types of pebbles were produced with this fabrication method, varying the amounts of cellulose fibers in the slurry from 5 to 15 wt% (total solids basis). Pebbles prepared using 5, 10, and 15 wt% of cellulose were denoted as P-5, P-10, and P-15, respectively.

2.2. Pebbles characterization

Thermal behavior of green pebbles was investigated by thermal gravimetric analysis (TGA) using a Q500 analyzer (TA Instruments, USA). Green pebbles were heated up from 30 to 950 °C in air with a constant heating rate of 10 °C/min. Crystallographic phase analysis of the sintered pebbles was conducted by X-ray diffraction (XRD) using a Bruker D2 Phaser powder diffractometer (Bruker Corporation, Billerica, MA, USA) with Cu-Kα radiation and a nickel filter equipped with a Bruker Lynxeye detector. The XRD patterns were recorded over a 2θ range between 10° and 65° with a scan speed of 0.02°/s. The particle size of green and sintered pebbles was estimated by using Matlab image

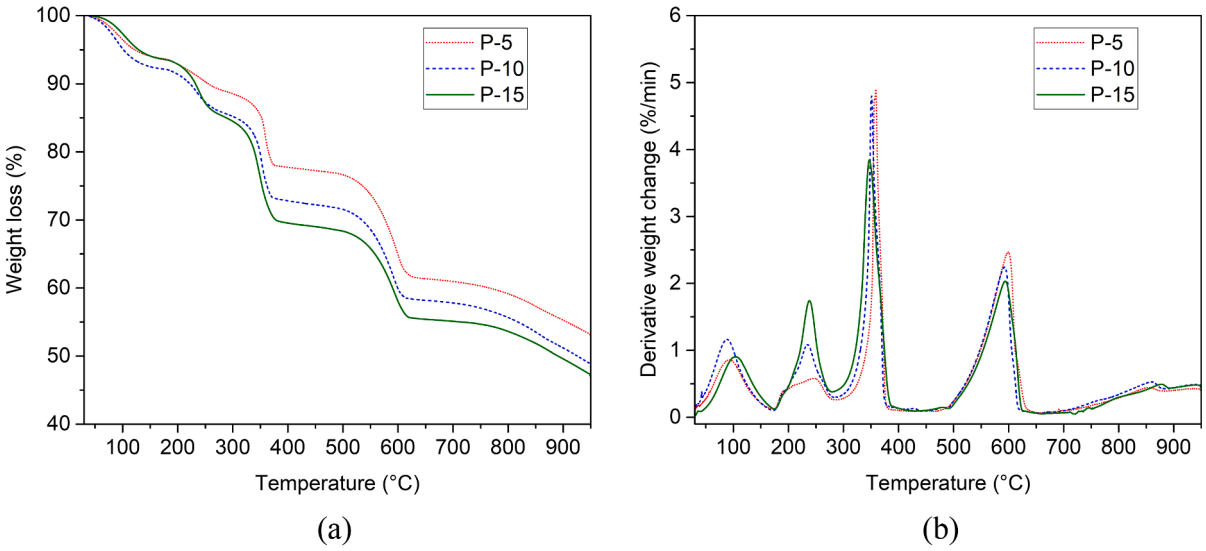

Fig. 3. Thermal behavior of green spheres with different cellulose fibers content: (a) TG, and (b) DTG curves in air.

processing tool, analyzing images of a statistical number of pebbles obtained by Eclipse 80i (Nikon Instruments Inc., USA) optical microscope. The pebbles microstructure after the thermal treatment was observed by scanning electron microscopy (SEM) using a FEI Quanta FEG 450 (FEI Inc., Hillsboro, OR, USA).

2.3. Pebbles compression tests

The force-displacement behavior of the pebbles has been investigated by means of crushing tests on single pebble at room temperature. Compression tests were carried out by using an Instron 5500R (Canton, MA, USA), equipped with a 100 N load cell, at a crosshead displacement rate of 100 μm/min. The pebbles were placed between two alumina cylinders before the execution of the test. For each sample a minimum of ten pebbles were tested, and the average values were reported.

3. Results and discussion

3.1. Thermal tests of green pebbles

The green pebbles produced with the drip casting method were characterized by TGA to determine the weight changes during the thermal treatment. The effect of temperature on the sintering process was observed by monitoring the weight of the samples. Fig. 3 shows the thermogravimetric (TG) and derivative (DTG) curves of green spheres (containing 5, 10, and 15 wt% of cellulose fibers) during the thermal treatment from 30 to 950 °C. In TG curves, four major weight losses were observed at four different temperature ranges, corresponding to significant peaks in the DTG curves. The first peak at around 100 °C is related to the loss of residual humidity in green pebbles. The total weight loss between 150 and 650 °C is about 30–40 % for all pebbles, and it could be attributed to the decomposition of organic compounds in the green pebbles. In the temperature range of 180–260 °C, the weight loss could be ascribed to a first decomposition of the Ca-alginate network, probably corresponding to the evolution of bonded water. The weight loss between 300 and 380 °C could be related to the cellulose fibers combustion, while between 500 and 600 °C the loss in weight could correspond to the combustion of Ca-alginate complexes [18]. At temperatures above 700 °C, a weight loss was observed, corresponding to a wide broad peak that could be ascribed to the reaction between the cross-linked compound (composed of Si-O-Si complexes) and LiOH to form Li_4SiO_4 phase, according to the reaction $4LiOH + SiO_2 \rightarrow Li_4SiO_4 + 2H_2O$.

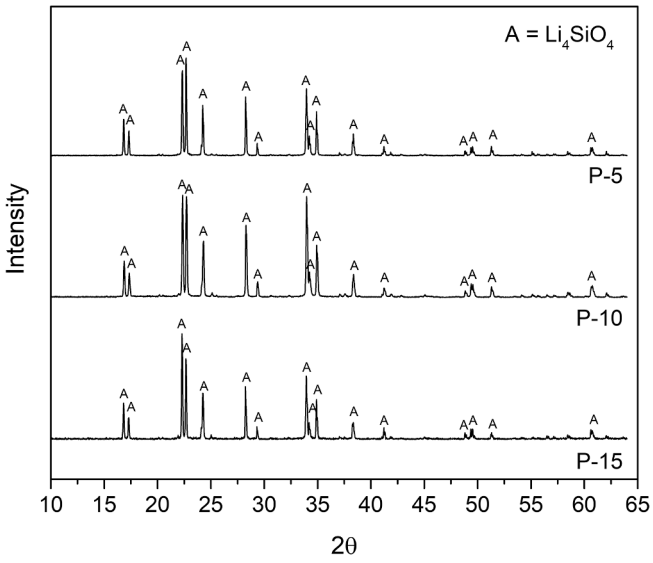

Fig. 4. XRD analysis results on pebbles produced with different slurry composition (5, 10, and 15 wt% of cellulose fibers).

3.2. Li_4SiO_4 pebbles characterization

The phase composition of the fabricated pebbles after the thermal treatment was studied by XRD analysis, the results of which are shown in Fig. 4. The diffractograms of all the pebbles display only the characteristic peaks of Li_4SiO_4 crystalline phase. Therefore, the thermal treatment allows the complete conversion of the sol–gel precursor into Li_4SiO_4 for all the green pebbles compositions.

Fig. 5 shows the green and the sintered pebbles that have been produced by means of the drip casting method; P-15 pebbles before and after the high-temperature thermal treatment are reported, as an example. The particle image analysis indicates that all the produced green pebbles resulted well-sized; they have the same sphericity grade and the dimensions are almost similar, with an average diameter of 2.1 mm (Fig. 5a). After the thermal treatment, the pebbles maintained their spherical shape (Fig. 5b), and a reduction in their diameter was observed due to the combustion of organic compounds in the green pebbles (alginate cross-linked structure and cellulose fibers). The average diameter for P-5, P-10, and P-15 pebbles (see Table 1) varies

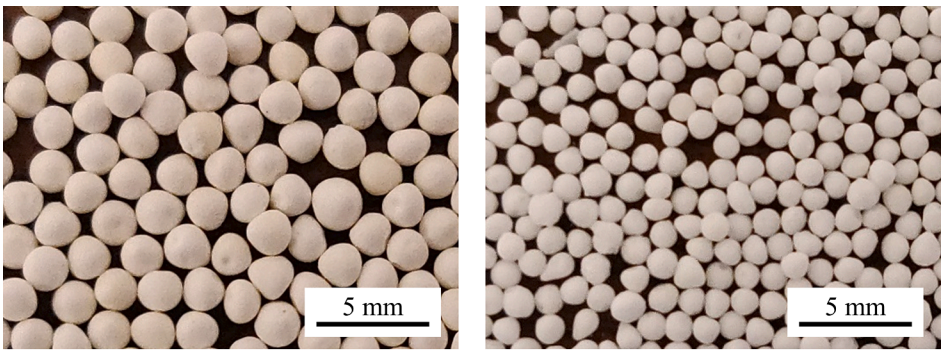

Fig. 5. Pebbles produced by drip casting method: (a) green P-15 pebbles (before the thermal treatment) and (b) sintered P-15 pebbles (after the thermal treatment).

Table 1
Average diameter, density (% of Li_4SiO_4 TD), and calculated linear shrinkage of sintered pebbles produced by drip casting method.

Sample Id.	Average diameter (mm)	Density (% TD*)	Linear shrinkage (%)
P-5	1.44	72	32.8
P-10	1.32	80	39.5
P-15	1.35	88	34.7

* TD = 2.326 g/cm^3.

between 1.32 and 1.44, and it is smaller for pebbles produced with 10 and 15 wt% of cellulose fibers. The calculated linear shrinkage ranging from 30 to 40 %. The relative density of the pebbles was evaluated by calculating the ratio between the apparent density of pebbles and Li_4SiO_4 theoretical density (TD = 2.326 g/cm^3). The apparent density was obtained by measuring the pebbles weight and calculating the equivalent volume by considering the average diameter obtained from the image analysis. As reported in Table 1, all the produced pebbles present high density (>70 %), that increase with increasing the amount of cellulose fibers added to the sol–gel suspension. P-15 pebbles reach a density value of 88 %, which is comparable to Li_4SiO_4 pebble density obtained with other fabrication processes [4].

The SEM morphological analysis of P-5, P-10, and P-15 pebbles is reported in Fig. 6. Images of the surface and cross-section at low magnification evidence that all the produced pebbles are not affected by macroscopic defects. Moreover, they exhibit homogeneous

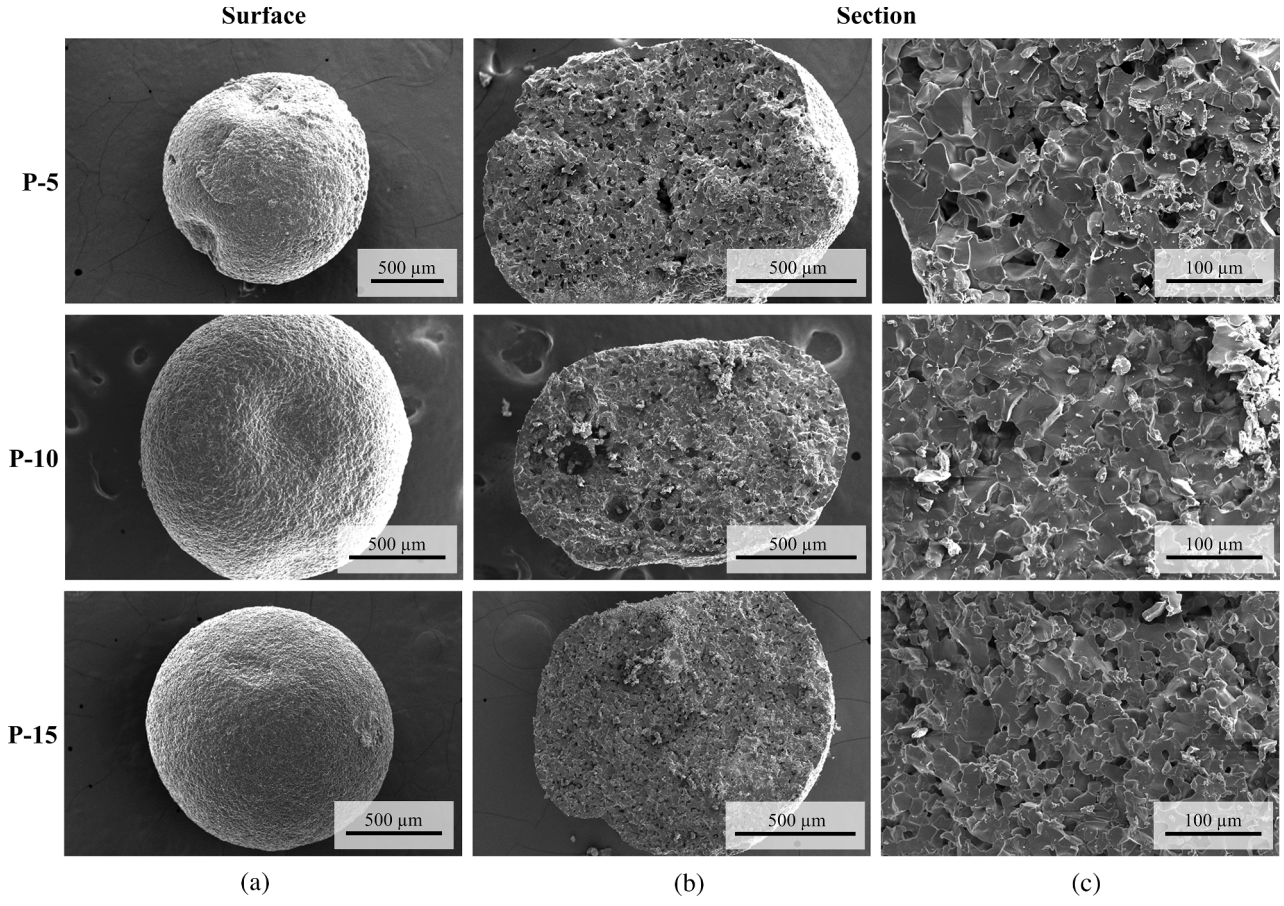

Fig. 6. SEM images of pebbles after the thermal treatment: (a) surface, (b) cross-section, and (c) detail of the pebbles internal microstructure at higher magnification.

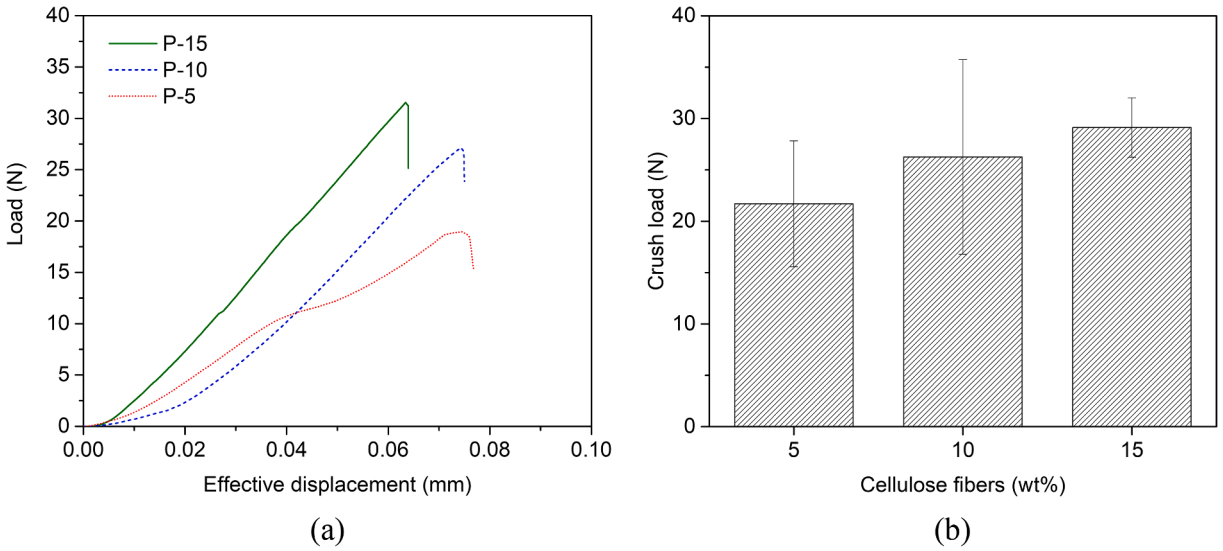

Fig. 7. Compression tests on Li_4SiO_4 pebbles: (a) load-displacement curves and (b) average crush load of pebbles produced with different slurry composition (5, 10, and 15 wt% of cellulose fibers).

microstructure of both surface and cross-section. SEM images of the pebbles cross-section at greater magnification (Fig. 6c) show a reduction in the internal porosity as the amount of cellulose fibers increases from 5 to 15 wt%. The grains appear fused together for all pebbles and no differences in the grain size can be observed. The porosity reduction observed by SEM is in agreement with the pebbles density (Table 1), which increases as the cellulose content increases. The microstructure densification for pebbles with higher cellulose content could be attributed to a thickening effect of cellulose fibers when the slurry is dripped to form droplets. This thickening effect is probably related to the interaction of cellulose fibers with silicates due to strong hydrogen bonds and van-der-Waals forces [19], which could promote particle aggregation.

3.3. Li_4SiO_4 pebbles compression tests

P-5, P-10, and P-15 pebbles after thermal treatment have been tested for crush load measurement. The results of compression tests are reported in Fig. 7. All the pebbles present a load–displacement curve typical of brittle materials. During the axial loading, the force is transmitted through a Hertzian contact area (assuming elastic the pebble behavior). The failure occurs when the load in circumferential directions exceeds the ultimate load value, forming cracks [20]. Average crush loads of 22, 26, and 29 N were measured for P-5, P-10, and P-15, respectively. Therefore, the compressive strength of pebbles produced by drip casting methodology is increased by increasing the cellulose fibers added to the sol–gel suspension. This enhancement in crushing load is due to the increase in pebbles density (as reported in Table 1 and discussed in section 3.2), which is related to the microstructure densification (Fig. 6) observed for increasing cellulose content. The obtained values are comparable to crush loads attained by bi-phasic pebbles [6,7,21], demonstrating the feasibility of the drip casting process for the production of breeder materials in pebble form.

4. Conclusions

In this work, a modification of the drip casting method for Li_4SiO_4 pebbles fabrication was presented. Different quantities of cellulose fibers (as thickening agent) were added to the sol–gel precursor suspension. The pebbles obtained after dripping, gelation, and sintering at high temperature presented regular roundness and same sphericity grade, Li_4SiO_4 high phase purity, and a homogeneous and dense microstructure. By varying the amount of cellulose fibers in the slurry from 5 to 15 wt%, the pebbles exhibited a reduction in the internal porosity, which corresponded to an increase in relative density (from 72 to 88 %) and compressive strength (crush load: 22–29 N). Further activities are planned to be performed for process optimization (systematic study of sintering step) and characterization of the produced pebbles (e.g. thermo-mechanical tests on pebble beds).

CRediT authorship contribution statement

Eleonora Stefanelli: Methodology, Investigation, Software, Writing – original draft, Writing – review & editing. **Monica Puccini:** Conceptualization, Methodology, Supervision, Writing – original draft. **Alessio Pesetti:** Software, Data curation. **Rosa Lo Frano:** Supervision, Writing – review & editing. **Donato Aquaro:** Supervision, Resources.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

[1] F. Hernández, P. Pereslavtsev, Q. Kang, P. Norajitra, B. Kiss, G. Nádasi, O. Bitz, A new HCPB breeding blanket for the EU DEMO: Evolution, rationale and preliminary performances, Fusion Eng. Des. 124 (2017) 882–886.
[2] M. Zmitko, P. Vladimirov, R. Knitter, M. Kolb, O. Leys, J. Heuser, H.-C. Schneider, R. Rolli, V. Chakin, S. Pupeschi, L. Magielsen, A. Fedorov, Y. Poitevin, Development and qualification of functional materials for the European HCPB TBM, Fusion Eng. Des. 136 (2018) 1376–1385.
[3] R.F. Mattas, M.C. Billone, Materials for breeding blankets, J. Nucl. Mater. 233-237 (1996) 72–81.
[4] R. Knitter, P. Chaudhuri, Y.J. Feng, T. Hoshino, I.-K. Yu, Recent developments of solid breeder fabrication, J. Nucl. Mater. 442 (1-3) (2013) S420–S424.
[5] R. Knitter, M.H.H. Kolb, U. Kaufmann, A.A. Goraieb, Fabrication of modified lithium orthosilicate pebbles by addition of titania, J. Nucl. Mater. 442 (1-3) (2013) S433–S436.
[6] Y. Gong, J. Li, S. Yang, M. Yang, H. Dang, Y. Ren, G. Zhang, T. Lu, Improvement of crushing strength and thermal conductivity by introduction of hetero-element Al into Li_4SiO_4, Ceram. Int. 45 (18) (2019) 24564–24569.
[7] O. Leys, M.H.H. Kolb, A. Pucci, R. Knitter, Study of lithium germanate additions to advanced ceramic breeder pebbles, J. Nucl. Mater. 518 (2019) 234–240.
[8] C. Dang, M. Yang, Y. Gong, L. Feng, H. Wang, Y. Shi, Q. Shi, J. Qi, T. Lu, A promising tritium breeding material: Nanostructured $2Li_2TiO_3$-Li_4SiO_4 biphasic ceramic pebbles, J. Nucl. Mater. 500 (2018) 265–269.

[9] Y. Gong, Z. Chen, M. Yang, H. Wang, C. Dang, W. Huang, T. Lu, A preliminary study on the preparation of nanostructured Ti-doped Li_4SiO_4 pebbles by two-step sintering process, Ceram. Int. 44 (14) (2018) 16209–16213.
[10] Y. Gong, J. Li, L. Liu, L. Xu, J. Cui, G. Zhang, T. Lu, Preparation of Li_4SiO_4 pebbles with increased lithium content and crush load via molten salt assisted sintering, Ceram. Int. 46 (14) (2020) 23282–23288.
[11] J.M. Heuser, M.H.H. Kolb, T. Bergfeldt, R. Knitter, Long-term thermal stability of two-phased lithium orthosilicate/metatitanate ceramics, J. Nucl. Mater. 507 (2018) 396–402.
[12] G. Jaya Rao, R. Mazumder, S. Bhattacharyya, P. Chaudhuri, Fabrication of Li_4SiO_4-Li_2ZrO_3 composite pebbles using extrusion and spherodization technique with improved crush load and moisture stability, J. Nucl. Mater. 514 (2019) 321–333.
[13] G. Jaya Rao, R. Mazumder, S. Bhattacharyya, P. Chaudhuri, Fabrication and characterization of Li_4SiO_4-Li_2TiO_3 composite ceramic pebbles using extrusion and spherodization technique, J. Eur. Ceram. Soc. 38 (15) (2018) 5174–5183.
[14] R. Lo Frano, M. Puccini, E. Stefanelli, D. Del Serra, S. Malquori, Manufacturing Technology of Ceramic Pebbles for Breeding Blanket, Materials. 11 (2018) 1–9.
[15] R. Lo Frano, M. Puccini, E. Stefanelli, M. Luppichini, C. Grima, S. Vitolo, D. Aquaro, S. Malquori, S. De Sanctis, Feasibility Study of a New Fabrication Method for the Li_4SiO_4 Pebbles, Proceedings of the 26th International Conference on Nuclear Engineering ICONE26, ASME, 2018: p. 5.
[16] R. Lo Frano, M. Puccini, E. Stefanelli, Feasibility study of a new fabrication method for the Li_4SiO_4 pebbles, International Conference on Nuclear Engineering, Proceedings, ICONE. 2 (2020) 1–6.
[17] R. Lo Frano, E. Stefanelli, M. Puccini, Feasibility of Li_4SiO_4 pebbles by drip casting and preliminary characterization, Fusion Eng. Des. 161 (2020), 111920.
[18] A.A. Said, R.M. Hassan, Thermal decomposition of some divalent metal alginate gel compounds, Polym. Degrad. Stab. 39 (3) (1993) 393–397.
[19] D. Van Opdenbosch, C. Zollfrank, Cellulose-based biotemplated silica structuring, Adv. Eng. Mater. 16 (2014) 699–712.
[20] Rosa Lo Frano, Donato Aquaro, Luca Scaletti, Thermo-mechanical characterization of ceramic pebbles for breeding blanket, Fusion Eng. Des. 109-111 (2016) 383–388.
[21] Y. Zeng, R. Chen, M. Yang, H. Wang, H. Guo, Y. Shi, Z. Huang, J. Qi, Q. Shi, T. Lu, Fast fabrication of high quality Li_2TiO_3–Li_4SiO_4 biphasic ceramic pebbles by microwave sintering: In comparison with conventional sintering, Ceram. Int. 45 (2019) 19022–19026.