Current Status of the Fabrication of Li$_4$SiO$_4$ and Beryllium Pebbles for CN HCCB TBM in SWIP

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Abstract Tritium breeder and neutron multiplier as functional materials play an important role not only in ITER test blanket module (TBM) but also in fusion reactor. The paper describes the status of the fabrication of the two materials in Southwestern Institute of Physics (SWIP). Li$_4$SiO$_4$ pebbles were fabricated by melt-spraying method. Most of the pebbles with the diameter of 1.0 mm are well spherically shaped. The properties of the pebbles have been investigated. The results show that the pebbles produced by this method have a high density of 93% TD (theoretical density). It was also found that the open/closed porosity will be decreased after thermal treatment, but the average crush load will be increased to 7 N. The rotating electrode process (REP) has been adopted to produce beryllium pebble for impurity control and mass production. The pebbles with the diameter of 1.0 mm were produced by REP. The beryllium pebbles produced by REP look almost perfectly spherical with a very smooth surface and a high density of 98% TD. The test results indicate that REP method has excellent prospects for the fabrication of beryllium pebbles and the attractiveness of their properties.

Keywords: Li$_4$SiO$_4$ pebbles, melt-spraying method, beryllium pebbles, REP

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1 Introduction

Worldwide research and development of functional materials have been directed toward application in DEMO. ITER testing of the as-developed materials will offer performance checks and initial screening of their use in a fusion blanket. The Chinese helium cooled ceramic breeder test blanket module (CN HCCB TBM) has been designed in SWIP (Southwestern Institute of Physics). Principal features of this TBM concept are the use of the lithium ceramic breeder and the beryllium multiplier in the form of pebble bed, which are separated and cooled by cooling plates. For the HCCB blanket, lithium orthosilicate (Li$_4$SiO$_4$) is considered as the reference breeding material and Beryllium is selected as the neutron multiplier [1]. Recently in China, great efforts have been dedicated to the development of fabrication techniques of breeder and beryllium pebbles.

There are many methods for the ceramic pebble fabrication [2–8], such as sol-gel, extrusion/spheronization, wet method, agglomeration and melt-spraying, etc. Fabrication of Li$_4$SiO$_4$ pebbles with average diameter of 1.2 mm was investigated by a water-based sol-gel technique [7]. The density of the Li$_4$SiO$_4$ pebbles was as high as 74% TD though the sintering temperature was as low as 900 °C. The fabrication of Li$_4$SiO$_4$ pebbles has been developed by wet method [8], which is a multistep process, including wet processing and sintering process. The pebbles have a small diameter of 0.5−0.8 mm, density of over 80% TD, high crush load of 20 N. Actually, sol-gel, wet method, extrusion/spheronization, and agglomeration all have granulation and sintering processes. The pebbles produced by these processes lead to low density and rough surface. These sintered pebbles loose easily powdered fractions during thermo cycling due to the surface roughness, and block the gas flow through the blanket canisters. And compared to the pebbles prepared by granulation and sintering, the pebbles produced from melting are closer to the spherical shape, have a smoother surface and a higher density. In the melt-spraying process of the pebbles the melt pot is supposed to be the only source of contamination. Therefore, the amount of impurities of the final products depends only on the impurities of the raw materials [9]. Thereby the impurities could be reduced so that a decreased waiting period for recycling was expected for the new materials. An additional advantage of the pebble fabrication by melting is its much simpler reprocessing. For the pebbles fabricated by a melt-spraying process, the direct remelting without any additional wet-chemical recycling step has been proposed as a simpler reprocessing process.

For the beryllium pebbles production, some meth-
ods have been proposed [9~12]: mechanical method, Mg reduction intermediate products, gas atomizing method, shot process and vacuum evaporation condensed method and rotating electrode process (REP). Mg reduction pebbles are intermediate products of beryllium production on commercial base. These pebbles are sorted out from large amount of Mg reduction crude metal. Impurity level is fairly high and the scatter in the quality distribution is large. In a gas atomizing process, the beryllium melt is prepared by induction melting and is poured into the nozzle. However, the particle shape is spherical with fairly wide size distribution. Among these production methods that have some merits and demerits, the REP has been expected to be suitable for impurity control and narrow particle size distributions.

This paper summarized recent studies on the fabrication of Li$_4$SiO$_4$ pebbles using the melt-spraying method and the fabrication of beryllium pebble using REP in SWIP. The properties of Li$_4$SiO$_4$ pebbles and beryllium pebbles are investigated.

2 Fabrication of Li$_4$SiO$_4$ pebbles

In the fabrication process, corundum crucible is used as the melt pot. The crucible is heated inductively. The crucible holds lithium carbonate and silica as raw materials, which are reacted and melted to liquid with Li/Si molar ratio of 4 according to stoichiometric. The raw materials are melted at temperature of about 1400°C. By spraying the molten liquid flow with a gas jet, hot droplets of irregular shape are formed. During flying through the air the hot droplets change their shape towards that of sphere due to surface tension, in the meantime the droplets are cooled down. The pebbles are sieved, only those with the size range of 0.8~1.0 mm are collected and further processed. Due to the rapid cooling of the droplets high stresses are formed in each pebble. Therefore, they are annealed at about 1000°C for 2 h to heal microcracks and to relieve internal stress. The current fabrication facility has the production capacity of 100 kg/year of Li$_4$SiO$_4$ pebbles with a diameter of 1.0 mm.

Fig. 1 shows the morphology and surface appearance of the pebbles. It can be seen from Fig. 1 that most of the pebbles are well spherically shaped, but in some cases there are smaller pebbles sticking to the surface of a larger pebble during the flight. Due to rapid cooling, the Li$_4$SiO$_4$ pebbles exhibit the known dendritic solidification microstructure. Fig. 2 shows the phase structure of the pebbles under different heat treatment conditions, as detected by X-ray diffraction (XRD). The diffraction peaks of Li$_2$CO$_3$, Li$_2$SiO$_3$, Li$_4$SiO$_4$ are observed in Fig. 2(a). This is because the carbon dioxide are easily absorbed by Li$_4$SiO$_4$ in the temperature range from 500°C to 720°C in ambient air. Fig. 2(b) shows the phase structure of the pebbles annealed in vacuum. Only the diffraction peaks of Li$_2$SiO$_3$, Li$_4$SiO$_4$ are observed. Li$_4$SiO$_4$ as the major phase and Li$_2$SiO$_3$ as a second phase were observed in the XRD patterns. It is clear that Li$_4$SiO$_4$ content will be more than 90 percent according to the XRD data. It can also be found that the Li/Si molar ratio is not equal to 4 due to the evaporation of lithium in molten state. For initial state pebbles, a density of 93.5% theoretical density (TD) and an open porosity of 5.7% were measured by Hg-prososimetry, the closed porosity of 0.8% was measured by He-pycnometry. After the heat treatment, the density is 94% TD, the open porosity, the closed porosity, the specific surface and the total pore volume for pores are all decreased (Table 1). It can be deduced that the heat treatment can heal microcracks and reduce the micro-pores.
maximum crush load is 16 N, with an average crush load of about 7.0 N. It reveals that the pebbles are virtually denser after the heat treatment, and the crush load of pebbles are scattered. Table 3 shows the results of chemical analysis of lithium orthosilicate pebbles. The Li/Si molar ratio is 3.94 as calculated from Table 3. The change of molar ratio are consistent with XRD data, this is because the evaporation of lithium at high temperatures. For the current pebbles, Al impurity of about 0.0017 wt% was measured, which is attributed to the raw materials and the crucible used in the melt-spraying process. The amount of impurities dominates the activation under neutron irradiation and also determines the necessary waiting period for the reprocessing. So, the impurities of the raw materials and all possible contaminations from the processing have to be considered carefully in future studies.

Table 1. Physical characteristics of Li$_4$SiO$_4$ pebbles

<table>
<thead>
<tr>
<th></th>
<th>Initial state</th>
<th>After heat treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (% TD)</td>
<td>~93.5</td>
<td>~94</td>
</tr>
<tr>
<td>Open porosity (%)</td>
<td>~5.7</td>
<td>~5.2</td>
</tr>
<tr>
<td>Closed porosity (%)</td>
<td>~0.8</td>
<td>~0.75</td>
</tr>
<tr>
<td>Specific surface area (m$^2$/g)</td>
<td>2.796</td>
<td>1.095</td>
</tr>
<tr>
<td>Total pore volume</td>
<td>3.403e–03</td>
<td>2.012e–03</td>
</tr>
</tbody>
</table>

Table 2. Crush load tests of Li$_4$SiO$_4$ pebbles

<table>
<thead>
<tr>
<th></th>
<th>Initial state</th>
<th>After heat treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Min. load (N)</td>
<td>4.3</td>
<td>5.2</td>
</tr>
<tr>
<td>Max. load (N)</td>
<td>12</td>
<td>16</td>
</tr>
<tr>
<td>Average load (N)</td>
<td>6.5</td>
<td>7.0</td>
</tr>
</tbody>
</table>

3 Fabrication of beryllium pebbles

The rotating electrode process (REP) was adopted to produce beryllium pebbles at SWIP in collaboration with a corporation. The REP facility is shown in Fig. 3. This method is essentially an arc melting the end of a long cylinder cast. The cast is rotating about its axis in a chamber filled with helium. Molten beryllium droplets are thrown off the end of the rotating cylinder and get solidified during flight. The size and quality of the REP beryllium pebbles depend essentially on the material used and on the production process parameters (e.g. electrode impurity content, electrode diameter, electrode angular velocity, cooling rate). The beryllium electrode was fabricated by vacuum hot pressing (VHP). The electrode was machined to $\Phi 33 \times 60$ mm by wire electrical discharge machining. The ductility of beryllium pebbles depends on Al and Mg impurities$^{[9]}$. They tend to segregate at grain boundaries since the low-melting phases influence the ductility of pebbles. Thus, if the impurity amounts are higher than the solubility limit, it is important that Al and Mg are tied up by impurities such as Fe and Si, to form solid intermetallic phases at high temperature. In order to form high temperature stable phases the produced beryllium pebbles have been annealed at 900 $^\circ$C for 1 h in vacuum furnace.

Fig. 3 REP facility for the fabrication of beryllium pebbles (color online)

Density of beryllium pebble measured by pycnometer is about 98% TD of beryllium. The specific surface measured by multipoint Brunauer-Emmett-Teller (BET) methods using nitrogen gas is 0.5449 m$^2$/g. The packing density was 1.115 g/cm$^3$ or $\sim$61% TD of beryllium. Table 4 shows the chemical composition of the beryllium pebbles. The purity of the pebbles depends essentially on the electrode used. From Table 4, the mass ratios of Al/Fe and Mg/Si in the Be pebbles are suitable in the present R&D phase.

Table 3. Chemical compositions of Li$_4$SiO$_4$ pebbles

<table>
<thead>
<tr>
<th>Element</th>
<th>Li$_2$O</th>
<th>SiO$_2$</th>
<th>Al</th>
<th>Na</th>
<th>Ti</th>
<th>Cu</th>
<th>Fe</th>
<th>Zr</th>
<th>Pb</th>
<th>Zn</th>
<th>Ca</th>
</tr>
</thead>
<tbody>
<tr>
<td>Content (wt%)</td>
<td>47.8238</td>
<td>52.06</td>
<td>0.0017</td>
<td>0.02365</td>
<td>0.0002282</td>
<td>0.00476</td>
<td>0.003887</td>
<td>0.000285</td>
<td>0.001492</td>
<td>0.000456</td>
<td>0.020008</td>
</tr>
</tbody>
</table>

Table 4. Chemical compositions of beryllium pebbles (wt%)

<table>
<thead>
<tr>
<th>Element</th>
<th>BeO</th>
<th>C</th>
<th>Fe</th>
<th>Al</th>
<th>Mg</th>
<th>Si</th>
<th>Other impurities</th>
</tr>
</thead>
<tbody>
<tr>
<td>Content (wt%)</td>
<td>0.9</td>
<td>0.12</td>
<td>0.07</td>
<td>0.03</td>
<td>0.01</td>
<td>0.02</td>
<td>0.04</td>
</tr>
</tbody>
</table>

293
Macroscopically, the beryllium pebbles with diameter of 1.0 mm look almost perfectly spherical with a very smooth external surface (Fig. 4). The optical microscopy of the pebbles shows an almost fully dense metallographic structure. Fig. 5 shows the SEM micrograph of beryllium pebble’s cross section. In Fig. 5, the pebble shows an almost fully dense metallographic structure characterized by the presence of large grains. However, some pebbles exhibit a big pore (up to 0.1~0.2 mm) at their center together with a fully dense region near the external surface. This kind of pebble structure is typical for a fabrication process with rapid cooling in gas atmosphere. Main features of the coolant process include: (1) rapid condensation of the liquid drop from the outer surface to the center, (2) frequent appearance of a big cavity in the center, and (3) grain boundaries in the radial direction and, as a consequence, grain diameters that strongly correlate with the pebble radius. From the observation that a bisection of pebbles also reduces the grain diameter by a factor of two, it can be preliminary concluded, that small pebbles are much more favorable to tritium release. In further studies, two possible factors will be considered. A possible method to decrease the grain size of the pebbles could be a further increase of the cooling rate of the molten beryllium. An option could be to add certain additives to the beryllium electrodes, which would work as nuclei of grains.

4 Conclusions

Current status of the fabrication techniques of Li$_4$SiO$_4$ pebbles and beryllium pebbles in SWIP are described. The Li$_4$SiO$_4$ pebbles produced by melt-spraying method are of high density with smooth surface. It was also found that after thermal treatment the crush load will be increased, and the open/closed porosity will be decreased. For the fabrication of beryllium pebbles, the REP method has been used successfully. The basic physical, chemical properties of beryllium pebbles have been studied. The results show that these pebbles satisfy the design requirements of CN HCCB TBM.

References

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