Consecutive Heat Treatment of Pre-lathed Pebble Fuel Elements for HTGR

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Abstract. In current manufacture process of pebble fuel elements for HTGR, the green pebbles were first carbonized, then lathed and purified at high temperature. The whole heat treatment process included two cycles of heating and cooling and corresponding two loading and unloading processes, which took approximately 90 hours in total. In order to reduce the time and energy consumed and improve the efficiency during the heat treatment process, a consecutive heat treatment process of pebble fuel elements for HTGR was established. In the newly established consecutive heat treatment process, the pebble fuel elements were carbonized and high temperature purified continuously in a specific furnace. The consecutive heat treatment process took less than 60 hours, which included only one cycle of heating and cooling and corresponding one loading and unloading process. Moreover, in order to recycle the matrix graphite powder after lathing, the green pebbles were machined to a certain size before suffering the heat treatment. However, in order to make the size of pebble fuel elements after the consecutive heat treatment meet the technical requirements, it is necessary to figure out their dimension changes during the heat treatment. As the pebbles were prepared by cold quasi-isostatic molding method, their dimension changes parallel and perpendicular to the molding direction were different. In order to better control the dimension changes of pebbles in the heat treatment process, the effects of physical properties such as apparent density, and particle size distribution of matrix graphite powder on the prepared pebbles were comparatively studied. Finally, the consecutive heat treatment of pre-lathed pebble fuel elements for HTGR was established. The comprehensive properties of pebbles prepared with the newly established consecutive heat treatment process satisfied all the technical requirements.

1. Introduction
HTGR fuel element designs commonly include two types: spherical fuel elements and prismatic fuel elements [1]. The former was first developed in Germany and then successfully applied in the AVR and THTR [2]. In China, the spherical fuel elements have been demonstrated in HTR-10 and will be used in HTR-PM soon [3, 4]. As one of the key technologies in the HTR-PM project, the prepared pebble fuel elements have been proved to satisfy the expected performances [5, 6]. In a pebble fuel element for HTR-PM, more than 95% in volume is the A3-3 matrix graphite (MG), which is composed of approximately 71 wt% natural flake graphite, 18 wt% artificial graphite, and 11 wt% phenol resin derived carbon [5, 7]. The fabrication process of pebble fuel elements for HTR-PM mainly includes four steps, namely, preparation of resinated matrix graphite powder, overcoating the TRISO-coated fuel particles, cold quasi-static molding, and carbonization, lathing, and high temperature purification [5].
After molding, the molded green pebbles were first carbonized at a maximum temperature of 800 °C, and significant weight loss and corresponding dimensional shrinkage occurred due to the decomposition of phenol resin [8]. The carbonized pebbles were lathed to diameter of 60 mm, and then subjected to high temperature purification under vacuum at 1900 °C. The whole heat treatment process of pebble fuel elements included two cycles of heating and cooling, and two corresponding loading and unloading processes, which took more than 90 hours in total. Meanwhile, the MG lathed from the carbonized pebbles could not be reused directly due to the decomposition of phenol resin in the carbonized MG during the carbonization. In order to recycle the lathed MG directly, the pebbles were lathed to a certain size and then suffered the heat treatment. Furthermore, in order to reduce the time and energy consumption throughout the heat treatment, a continuous heat treatment equipment and corresponding process were designed and developed. The newly developed consecutive heat treatment process took less than 60 hours and included only one cycle of heating and cooling, and corresponding one loading and unloading process. With careful control of physical properties of A3-3 MG powder such as apparent density and particle size distribution, the dimensions and other comprehensive properties of pebbles prepared with the newly continuous heat treatment process met all the technical specifications.

2. Experimental

2.1. Raw Materials
As more than 90% either in volume or in mass of pebble fuel elements for HTR-PM is A3-3 MG, the comprehensive properties of fuel pebbles are commonly investigated with MG or MG pebbles instead of the fuel pebbles. Green pebbles were prepared in INET [5] with qualified raw materials such as natural flake and artificial graphite powders, and phenol resin. The resinated MG consists of 64wt% natural flake graphite powder, 16wt% artificial graphite powder, and 20wt% phenol resin.

2.2. Property Measurement
The measurement of bulk density and tap density of resinated MG strictly complied with Chinese Standards GB/T 16913.3-2008 [9] and GB/T 5162-2006 [10], respectively. The equipment for testing bulk density and tap density is produced by Bettersize Instruments Ltd. Each sample was tested three times and the average was taken as the final result. The particle size distribution of MG was measured using the e200LS air sieve produced by Alpine company. Screens with mesh size of 32µm, 63µm, 160µm, 400µm, and 800µm were selected. In every test of each screen, 10 grams of MG sample were sieved for 5 minutes under the operating negative pressure of 2000 Pa. For instance, the weight of screen with mesh size of 32µm is $W_1$. After sieving under the above conditions, the total weight of the screen and the MG sample left on the screen was $W_2$. The percentage of particle size distribution of less than 32µm ($PSD_{32}$) could be calculated by the following eq. 1.

$$PSD_{32}=100\times\left(1-\frac{W_2-W_1}{10}\right)$$

The comprehensive properties of MG pebbles such as crush strength, thermal conductivity, anisotropy of CTE, corrosion rate and erosion rate were tested in strict compliance with the measurement procedures which were introduced in detail elsewhere [11].

2.3. Continuous heat treatment equipment
The schematic of newly designed continuous heat treatment equipment was shown in Fig. 1. The equipment mainly includes furnace body (1, 13 in Fig. 1), heating and insulation system (2,3,4), loading and unloading system (5, 6), vacuum system (11, 12), exhaust gas exhaust system (8, 9), process gas circuit system (7), cooling water system, exhaust gas combustion system (10) and electrical control system. The furnace body has a horizontal structure, and the front and rear furnace doors are provided with a heat shield layer that can be opened and closed. The heating and insulation system consists of graphite heating element (4), insulation layer (3) and steel furnace liner (2) from the inside to the outside.
The loading and unloading system are inside the heating and insulation system, which is composed of graphite muffle box and loading plates. The loading capacity is around 500 pebbles. The carbonization of pebbles is carried out under argon atmosphere with a slightly positive pressure. In order to prevent the volatile decomposition products from entering the heating and insulation system and allow the decomposition products to be directed through the exhaust system, the process inlet gas is introduced from different directions outside the graphite muffle box, and the exhaust gas is discharged through the only outlet at the bottom of the graphite muffle box, which connects the exhaust pipe (8) and exhaust gas combustion system (10). The macromolecular products in the decomposition products are condensed and collected in the exhaust pipe, while the gaseous products at room temperature go through the valve (9) into the combustion system and are oxidized to water and carbon dioxide. The valve can automatically adjust the degree of opening and closing to ensure a stable slightly positive pressure in the furnace.

The furnace must be evacuated before carrying out the high-temperature purification. The vacuum system mainly consists of two vacuum pumps (12) and vacuum pipe (11) which connects the pumps and the furnace. During the entire high-temperature purification process, the vacuum pump must be kept on to continuously vacuum the furnace.

The equipment can not only perform carbonization or high-temperature purification of pebble fuel elements separately, but also carry out the continuous heat treatment of carbonization and high-temperature purification for pebble fuel elements. After the MG pebbles were placed on the graphite plates in the graphite muffle box, the furnace door was closed and the furnace was evacuated to less than 300 Pa. Subsequently, the furnace was filled with argon gas to a slightly positive pressure and heated up to start the carbonization process. The MG pebbles were slowly heated to 800 °C under argon atmosphere of a slightly positive pressure and kept at 800 °C for 1 hour. It took approximately 28 hours for the total heating and holding during the carbonization process. Unlike the direct cooling down after the holding at 800 °C was completed in traditional carbonization process, the furnace was evacuated and further heated up to at the maximum of 1900 °C to carry out the high-temperature purification under vacuum of less than 50 Pa for the continuous heat treatment. It took around 10 hours to run the high-temperature purification process.

After the high-temperature purification process was completed, the furnace was cooled down and the pumps kept operating until the temperature of furnace was low than 1000 °C. Argon was introduced into the furnace to improve the cooling efficiency. When the furnace temperature was lower than 600 °C, the heat shielding door inside the front and rear doors was opened to further enhance the cooling rate at relatively low temperature of furnace. Through the above measures, it took only about 20 hours for the furnace temperature to drop from 1900 °C to 100 °C, at which it was allowed to open the furnace door. Finally, the MG pebbles treated with the continuous heat treatment were unloaded. The entire continuous heat treatment took less than 60 hours, which was around 30 hours shorter than the common heat treatment process where the carbonization and high-temperature purification was carried out separately.

![Figure 1. Schematic of continuous heat treatment equipment](image-url)
3. RESULTS AND DISCUSSIONS

3.1. Characterization of A3-3 MG powder

The resinated A3-3 MG powder is composed of 64wt% natural flake graphite powder, 16wt% artificial graphite powder, and 20wt% phenol resin. Firstly, the natural graphite powder and artificial graphite powder are mixed in a conical mixer. The mixture is then fed into a kneading machine where phenol resin, dissolved in ethanol, is added and the mixture is homogenized in order to achieve the homogeneous dispersion and adhesion of resin onto the surface of graphitic particles. The homogeneous paste-like mixture is extruded through a punched screen creating strings that are cut into small pieces. These small pieces are then placed in drying trays and heated to ~100 °C under vacuum to remove the ethanol in the mixture. A hammer mill is used to grind the dried mixture into powder with the desired apparent density of 0.51-0.55 g/cm$^3$. Finally, the milled powder is homogenized and the resinated A3-3 MG powder are prepared.

In order to comparatively study the specific characteristics of MG powder on the dimension changes of MG pebbles throughout the heat treatment, two batches of MG powder were prepared. The average apparent density of MG powder 1 and 2 are 0.513 and 0.545 g/cm$^3$, respectively. The mean tap density of MG powder 1 and 2 are 0.793 and 0.817 g/cm$^3$. The Hausner ratio, i.e., the ratio of tap density to apparent density, of MG powder 1&2 are 1.55 and 1.50, respectively. The ratio of the two MG powders is greater than 1.50, which indicates their poor fluidity. The higher the ratio, the worse the fluidity. Therefore, the fluidity of MG powder 2 is slightly better than that of MG powder 1. The measured particle size distribution (PSD) of MG powder 1&2 is listed in Table 1. It can be seen that nearly half of MG powder 1 has a particle size below 32 µm and more than 95wt% of MG has a particle size of less than 800µm. The particle size of MG powder 2 is larger than that of MG powder 1, which coincides well with the apparent density.

| PSD  | MG powder-1 wt% | MG powder-2 wt% |
|------|----------------|----------------|
| <32µm| 44.37          | 34.78          |
| <63µm| 62.95          | 50.10          |
| <160µm| 73.17         | 62.13          |
| <400µm| 85.20          | 79.23          |
| <800µm| 95.91          | 94.35          |

3.2. Shrinkage of MG pebbles

Using cold quasi-isostatic molding method, green MG pebbles were fabricated with the prepared A3-3 MG powder 1&2, respectively. The green pebbles were lathed to a certain dimension and then suffered the continuous heat treatment of carbonization and high-temperature purification. As shown in Table 2, the dimensions parallel and perpendicular to the molding direction of MG pebbles before and after the continuous heat treatment were measured and calculated to obtain the average dimensional shrinkage rate.

|                | MG powder 1 | Average shrinkage | Deviation |
|----------------|-------------|-------------------|-----------|
| Parallel       |             | 2.3%              | 0.08%     |
| Perpendicular  |             | 1.3%              | 0.06%     |
| MG powder 2    |             |                   |           |
| Parallel       |             | 1.9%              | 0.07%     |
| Perpendicular  |             | 1.1%              | 0.05%     |
From Table 2, it can be seen that the shrinkage rate of MG pebbles made of MG powder 1&2 parallel to the molding direction is higher than that perpendicular to the molding direction. The difference in shrinkage between the two orthogonal directions is mainly due to the quasi-isostatic molding brought by the silicon rubber die. During the molding process, the pressure applied on the steel sleeve was transmitted to the pebble through the silicon rubber. Because the silicon rubber is not a complete fluid, the pressure transmission during molding is anisotropic. Namely, the pressure suffered by the pebble parallel to the molding direction is higher than that perpendicular to the molding direction. As a result, the shrinkage rates of MG pebbles made of MG powder 1 either parallel or perpendicular to the molding direction are higher than those made of MG powder 2, which is probably due to the relatively smaller PSD of MG powder 1. From our point of view, the shrinkage of pebbles containing fuel particles should be lower than that of matrix graphite pebbles.

### 3.3. Comprehensive properties of MG pebbles

In order to further verify the shrinkage rate of MG pebbles throughout the continuous heat treatment, a new batch of MG powder 3 was prepared. The apparent density of MG powder 3 is 0.531g/cm³ and its PSD lies between MG powder 1&2. A batch of 50 MG pebbles were manufactured with MG powder 3. According to the shrinkage rate listed in Table 2, the average shrinkage rate parallel and perpendicular to the molding direction, i.e., 2.1% and 1.2% were used as references. Correspondingly, the dimension parallel and perpendicular to the molding direction of green MG pebbles were machined to 61.3 mm and 60.7 mm, respectively. The expected orthogonal dimensions of MG pebble should be approximately 60.0 mm after the heat treatment. Then these MG ellipsoids were suffered the continuous heat treatment of carbonization and high-temperature purification in the specific furnace mentioned above. The average dimension and its corresponding deviation parallel and perpendicular to the molding direction were 59.96±0.05 mm and 60.03±0.04 mm, respectively. The orthogonal dimensions of all the 50 MG pebbles were in the range of 59.9-60.1 mm, which totally met the technical requirement of 59.6-60.2 mm. The comprehensive properties of MG pebbles were presented in Table 3. It can be seen that the physical, mechanical, thermal, and chemical properties of the MG pebbles manufacture with the continuous heat treatment process totally satisfy the specification requirements.

| Item                               | Specification | Mean value |
|-----------------------------------|---------------|------------|
| Density (g/cm³)                   | [1.70-1.77]   | 1.75       |
| Number of drops a                 | ≥50           | ≥50        |
| Crush strength (kN)b              | ≥18           | 21.5/26.7  |
| Thermal conductivity (@1000, W/m K)| ≥25.0       | 31.8       |
| CTE anisotropy (20-500°C, α⊥/α//) | ≤1.3         | 1.16       |
| Corrosion rate (mg/cm² h)c        | ≤1.3         | 0.76       |
| Erosion rate (mg/h)               | ≤6.0         | 1.62       |

a Number of drops from 4m high onto the pebble bed before break.
b Parallel and perpendicular to the molding direction.
c @1000°C, 10h, atmosphere is Helium+1vol% H₂O.

### 4. Conclusion

Based on the newly developed furnace, a continuous heat treatment process including the carbonization and high-temperature purification was established. With the stringent control of properties such as particle size distribution and apparent density of MG powder, the green pebbles molded by quasi-isostatic molding method were lathed to a certain size before the continuous heat treatment. The dimension and comprehensive properties of MG pebbles treated with the newly established continuous heat treatment process totally satisfied the technical requirements. Comparing with the heat treatment carried out separately, the continuous heat treatment process took less than 60 hours, which significantly
improved the efficiency and reduced the energy and time consuming. Moreover, it also provided the potential for the recycling and reusing of the matrix graphite powder produced in the lathing process.

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