1. Introduction

As a new energy resource, shale gas exploration and development cause high environmental risks as approximately 250 m^3 of oil-based drill cuttings are generated by one well [1]. Pyrolysis is typically performed for oily solid wastes to maintain the oil content within 0.3% and facilitate a solidification process [2]. After the solidification with cement, the absolute majority of contaminants in drill cutting pyrolysis residues (DCPR) form solidified blocks [3–6]; however, it does not mitigate the pollution caused by oil and heavy metals. By conducting a sintering process, oil can be burned while heavy metals become solidified in crystals.

High-quality kaolin, bauxites, and refractory clays are natural raw materials traditionally used for the production of aluminosilicate ceramic proppants [7,8], while natural and artificial additives are utilized to promote the sintering process and increase the strength of the final product [9–15]. However, owing to the scarcity and gradual depletion of high-quality clays and kaolin, low-grade clays (so-called brick clays) are widely used for the preparation of LWAs [16,17]. It is well known that the mechanical strength of ceramics primarily depends on their crystal structure [18], phase composition [19], and sintering characteristics (density and porosity) [20]. Previous studies describing the use of certain igneous rocks, such as basalt rocks [21–23], granites, and diabase [24–26], in ceramic brick technology have confirmed their effects by increasing the total content of the crystalline phase. For example, Jiang et al. [27] reported that the leaching rate of aluminabased ceramic core materials containing silica fibers was relatively high.

According to the GB/T 17431.2–2010 standard [28], in addition to high compressive strength (above 3.6 MPa), LWAs should also possess sufficiently small particle and bulk densities (below 1200 kg/m^3). In the modern ceramics production process, a material melt intercepts a gas generated at high temperature; as a result, ceramite expands to form a porous structure, which decreases its density [29–31]. SiO_2 and Al_2O_3 are the main components of crystals, while Na_2O, K_2O, CaO, Fe_2O_3, and MgO contribute to fluxing, which can effectively reduce the crystal melting temperature and liquid-phase viscosity. Compared with SiO_2 and Al_2O_3, fluxing changes the liquid-phase viscosity to intercept the gas during sintering. To determine the ability of materials to produce sintered aggregates, the SiO_2/flux and (SiO_2 + Al_2O_3)/flux mass ratios are calculated. Specifically, SiO_2/flux should be greater than two, and (SiO_2 + Al_2O_3)/flux must be between 3.5 and 10 [31,32]. Riley [33] and Cougny [34] drew expansion areas in the Al_2O_3/flux vs. SiO_2 and Fe_2O_3/Al_2O_3 vs.
MgO + CaO + Na₂O + K₂O coordinate systems, respectively. In addition, Cougný determined the optimal particle size distribution range for LWA expansion. Carbonates [35–38], SiC [39,40], CaSO₄ [41], eggshell [42,43], basalt scoria [44], and Pb–Zn mine tailings [45] are widely used as foaming agents with good expansion properties [46]. However, alkali activation combined with mechanical stirring also enhances the expansion process [47–50]. Wie et al. suggested that sintering time significantly influenced the expansion process [51] and then provided a chemical design, in which shells and cores with different melting points effectively suppressed the adhesion of aggregates [52].

As of today, no mainstream resource utilization methods for DCPR have been developed, which led to DCPR hoarding. Because the properties of DCPR are similar to those of shale, they contain large amounts of SiO₂ and Al₂O₃ and exhibit good sintering characteristics, demonstrating high potential for sintered ceramic lightweight aggregates.

2. Materials and methods

2.1. Materials

Oil-based drill DCPR were collected from a pyrolysis treatment station of a shale gas survey company located in Chongqing, China. They contained a gray-black solid powder mixed with a small amount of gravel, metal wire, and other impurities. Shale (SHA), a reddish-brown solid powder, was provided by a ceramic aggregate production company in Chongqing, China, and fly ash (CFA) was purchased from Henan Hengyuan New Material Company. All powders were passed through a 200-mesh sieve (φ < 74 mm) before use. The purity of SiC was 99.7%.

2.2. Characterization

X-Ray diffraction (XRD) patterns (Figure S1) show that DCPR and SHA have similar phase compositions. In the shale gas mining process, BaSO₄ was added to the drilling fluid as a weighting agent. Therefore, the XRD spectrum of DCPR contains the characteristic BaSO₄ peaks. Figure S1(b) displays the XRD spectrum of CFA, which was produced by melting SiO₂ and Al₂O₃ in the incineration process followed by the formation of mullite crystals (3Al₂O₃·2SiO₂) through restructuring.

X-ray fluorescence spectroscopy (XRF) was performed to analyze the chemical compositions of the studied samples (Table 1).

2.3. Wt/%: mass percentage

The chemical composition of DCPR shows that it can be potentially used to prepare ceramic LWAs. However, the contents of SiO₂ and Al₂O₃ in DCPR are relatively low, which results in a simple crystal structure with low strength after sintering. Meanwhile, SHA and CFA contain high amounts of SiO₂ (60.07%) and Al₂O₃ (31.93%). Therefore, they were used to adjust the content of SiO₂ and Al₂O₃ in the raw materials. In DCPR, the content of fluxing components (Fe₂O₃, CaO, MgO, Na₂O, and K₂O) reached 24.19%, which could reduce the crystal melting temperature, increase the liquid-phase fluidity, and promote the reorganization of the crystal structure to form aluminosilicates, thereby decreasing the sintering temperature. Among these components, the content of CaO was 14.07%, which played the most significant role in the fluxing process.

The thermogravimetric (TG) curves of DCPR, CFA, and SHA recorded during heating from 25 to 1200°C and the corresponding differential scanning calorimetry (DSC) curves are presented in Figure S2. Between room temperature and 200°C, the sample mass loss was dominated by the loss of free water, while in the range of 400–700°C, the mass loss was mainly due to the decomposition of CaCO₃. In the temperature range of 300–600°C, residual organic matter oxidized to generate heat, resulting in an exothermic peak in the DSC curve of DCPR. Above 900°C, after DCPR and SHA absorbed a large amount of heat, the covalent bonds in the crystal structure were broken, the crystal melted, and a liquid phase was formed, which decreased the heat flow in the corresponding DSC curves. In contrast, the descent of the DSC curve of CFA occurred relatively late (at 1100°C) owing to the high thermal stability of mullite crystals. Because DCPR is a shale powder containing a small amount of the residual drilling fluid and metal fragments and its main components are similar to those of shale, the TG–DSC curves of DCPR are nearly identical to those of SHA. Above 1100°C, the TG curve of DCPR descends again, whereas its DSC curve exhibits an increasing trend. This occurred because BaSO₄ decomposed at this stage to produce SO₂ gas, resulting in a mass loss.

2.4. Preparation process

As shown in Table 2, CFA and SHA were added to the raw materials to increase their SiO₂ and Al₂O₃ contents. After the raw materials were mixed according to the ratios provided in Table 2 and stirred thoroughly,
deionized water was added at the dry material: water = 4:1 ratio to produce spheres with diameters of approximately 1 cm. The prepared spheres were placed in an electric heating blast drying box and dried at 105°C under ventilation for 12 h to prepare bodies for the firing process. The green bodies were placed into a muffle furnace, heated to 1050/1075/1100/1125/1150°C at a rate of 10°C/min, and sintered for 10 min. Finally, the sintered LWAs were quickly taken out of the furnace and cool down to room temperature in air.

### 2.5. Fluxing: CaO + MgO + Na2O + K2O + Fe2O3

According to the results obtained by Ren et al. [31] and Gennaro et al. [32], ceramsite possesses good expansion properties when SiO2/Σflux is greater than 2, and (SiO2+ Al2O3)/Σflux is between 3.5 and 10. Hence, the SiO2/Σflux and (SiO2+ Al2O3)/Σflux of spheres were calculated via the following formulas:

\[
I = \frac{SiO2}{\sum \text{flux}} = \frac{m_{SiO2}}{m_{CaO} + m_{MgO} + m_{K2O} + m_{Na2O} + m_{Fe2O3}}
\]

\[
R = \frac{(SiO2 + Al2O3)}{\sum \text{flux}} = \frac{m_{SiO2} + m_{Al2O3}}{m_{CaO} + m_{MgO} + m_{K2O} + m_{Na2O} + m_{Fe2O3}}
\]

Based on the obtained results, the ceramic composition was optimized, and expansion experiments were conducted.

In this study, SiC was selected as an expansion agent. In the expansion experiment, SiC was added at concentrations of 2.5% and 5.0%, and the generated gas created a porous structure and thus reduced the LWA density.

For each formulation, three parallel tests were conducted under each sintering condition, and the average value of these tests was taken as the final result.

### 2.6. Detection methods

To quickly measure the compressive strength of the produced aggregates, a particle strength meter (KY-20, China; maximum value: 1000 N) was applied to record the ultimate load, which corresponded to the maximum load causing their rupture. Five samples were tested out randomly for each group of LWAs, and the final ultimate load was represented by their average value. By performing visual observations, surface color, gloss degree, and the degree of glaze on the ceramsite surface were determined. LWAs with severe structural collapse and surface damage due to excessive sintering were defined as the molten form.

Each group of LWAs was weighed after sintering, and their water absorption and apparent density were estimated according to the GB/T 17431.2–2010 standard [53]. After soaking in pure water for 1 h, LWAs were taken out and rolled back and forth on a wet towel 8–10 times, after which the water attached to the body was removed. The LWAs were weighed again to calculate the one-hour water absorption as follows:

\[
A = \frac{m_{w} - m_{0}}{m_{0}} \times 100%
\]

Where \( A \) is the water absorption, \( m_{w} \) is the mass of ceramic aggregates with absorbed water, and \( m_{0} \) is the mass of the raw ceramic aggregates.

Next, wet LWAs were placed in a 50-mL graduated cylinder followed by the addition of 25 mL of water. The apparent density of LWAs was calculated via the following formula:

\[
\rho_{b} = \frac{m_{0}}{V \times 25} \times 1000
\]

Where \( \rho_{b} \) is the apparent density, and \( V \) is the volume of water with wet ceramic aggregates.

For the final products, compressive strength and bulk density tests were performed according to the GB/T 17431.2–2010 standard [53]. A hydraulic press (MTS 815) increased the load on the LWAs in the pressure vessel at a constant speed of 300 N/s, and the pressure value was recorded when the pressing depth of the stamping die reached 2.0 mm:

\[
f_{a} = \frac{p_{1} + p_{2}}{F}
\]

Where \( f_{a} \) is the compressive strength (MPa), \( p_{1} \) is the load (N), \( p_{2} \) is the stamping die mass (N) (\( p_{2} = 18.33 \) N), and \( F \) is the bearing area (\( F = 10000 \) mm²).

After LWAs naturally fell into a 1-L vessel, the sample at the upper part of the capacity cylinder assumed a conical shape. Subsequently, it was scraped with
a ruler along the edge of the capacity cylinder from the center to both sides, and the surface depressions were filled with aggregates of smaller sizes. Bulk density was calculated as

$$\rho_{bu} = \frac{(m_t - m_v) \times 1000}{V}$$

Where $\rho_{bu}$ is the bulk density (kg/m$^3$), $m_t$ is the mass of the sample and vessel (g), $m_v$ is the mass of the capacity cylinder (g), and $V$ is the vessel capacity (1000 mL).

A thermogravimetric analyzer (TGA/DSC1/1600LF) was used to evaluate the thermodynamic properties of the samples, and the obtained TG curves characterized the mass change of the sample during the heating process. Combined with the heat flow DSC curves, the enthalpy changes ($\Delta H$) of the samples during heating were obtained to determine chemical reaction types at different temperatures.

A desktop scanning electron microscope (TM-4000 Plus) was used to observe the LWA morphology. A field emission transmission electron microscope (Talos F200S) manufactured by Thermo Fisher Scientific was utilized to obtain the crystal structure, while its energy-dispersive spectroscopy (EDS) module was employed to determine the elemental distributions in the studied samples.

### 3. Results and discussion

#### 3.1. Characteristics of LWAs

Among the oxide components of the studied samples, CaO is the main melting aid. In addition, Ca element plays an important role in the formation of aluminosilicate crystals during sintering. For the $\text{SiO}_2$–$\text{Al}_2\text{O}_3$–CaO spheres prepared at different ratios of the raw materials, a ternary diagram was constructed after normalization (Figure 1(a)). Because of their high CaO content, DCPR are located in the closest region to the liquid-phase region (A5lag-liq) and thus easily melt during sintering. The liquid phase has the lowest viscosity and highest fluidity. However, it also tends to produce a glass phase, which increases the internal stress of the material and ultimately decreases the compressive strength of LWAs. With the addition of SHA and CFA, the corresponding points in the diagrams gradually moved away from the liquid-phase region. During the sintering process, the amount of the produced melt decreased, the liquid-phase viscosity increases, and its fluidity decreased. As a result, the process requirements for ceramic-forming samples were satisfied, and anorthite crystals with a complex structure were formed after sintering, which increased the LWA strength. Note that the BaO phase in DCPR plays a role similar to that of CaO in the formation of aluminosilicate crystals, and the produced crystal phase resembles a complex silicon aluminate $\text{MA}_2\text{Si}_2\text{O}_6$ ($M = \text{Ba}$ or Ca) phase.

The black circle in Figure 1(b) shows the expansion area of the clay LWAs sintered at 1260°C [31]. In the temperature range of 1050–1150°C, the melt amount decreases, and the liquid-phase viscosity increases; as a result, the expansion area shifts toward the fluxing phase. Therefore, PRFA and PRS LWAs exhibited good expansibility.

The average particle strength of LWAs was measured by the particle strength meter, and the obtained results are listed in Table 3.

When the sintering temperature was 1100°C and lower, both the particle strength and degree of glaze increased with an increase in the sintering temperature. The average ultimate load of PRFA and PRS exceeded 1000 N at sintering temperatures of 1100 and 1075°C, respectively, and the average ultimate load of PRFA in this temperature range was systematically lower than that of PRS. When the sintering
Table 3. Ultimate loads and degrees of glaze determined for ceramic aggregates.

| Strength (N) | 1050°C | 1075°C | 1100°C | 1125°C | 1150°C |
|--------------|--------|--------|--------|--------|--------|
| ODPR         | 179.27 ± 53.93 N | 339.28 ± 48.32 L | 878.56 ± 103.42 M | ±1000 H | ±1000 H |
| PRFA20       | 342.98 ± 163.67 N | 740.5 ± 99.12 N | >1000 L | >1000 L | >1000 L |
| PRFA40       | 373.54 ± 44.70 N | 689.38 ± 141.35 N | >1000 L | >1000 L | >1000 L |
| PRS20        | 596.6 ± 132.53 N | >1000 L | >1000 H | >1000 H | 453.32 ± 44.46 M |
| PRS40        | 473.78 ± 91.06 N | >1000 L | >1000 H | >1000 H | 596.48 ± 96.89 M |

N: not glazed, L: slightly glazed, H: severely glazed, M: melt

temperature was higher than 1100°C, the degree of glaze of the LWA surface increased considerably. At 1150°C, the LWAs of the PRS and DCPR samples melted and lost their original shape. Among these samples, the DCPR LWAs were severely melted, stuck inside the container, and could not be tested. The average ultimate loads of PRS20 and PRS40 decreased to 453.32 and 596.48 N, respectively. The LWA particle strength varied with the sintering temperature, and the observed process was divided into two stages. At the first (strengthening) stage, as the sintering temperature increased, the amount of melted LWAs increased, and a glass phase was formed after the cooling process. The larger amount of the glass phase enhanced the stickiness effect of crystal particles; therefore, the LWA particle strength increased. The second stage was an over-melting stage. When the sintering temperature exceeded the temperature corresponding to the maximum strength of LWAs, both the melt and glass phase amounts increased after cooling down. Owing to the higher internal stress of LWAs and lower fraction of crystal particles, the average particle strength of LWAs was reduced.

The degree of glaze of the LWA surface strongly affected its water absorption properties. Figure 2(a) shows the one-hour water absorption trends of various LWA groups sintered at different temperatures. In the temperature region of 1050–1150°C, the water absorption rates of PRS20 and PRS40 decreased from 13.40% and 14.21% to 1.02% and 1.17%, respectively, without significant changes afterward. Meanwhile, the loss on ignition (LOI) values of the studied materials were influenced by the addition of CFA and SHA (Figure 2(b)). Compared to DCPR, the LOIs of these groups did not vary significantly with temperature.

At the fast-melting stage between 1050 and 1075°C, the maximum absolute value of the water absorption curve slope was observed (0.39 and 0.33, respectively). The water absorption rate of PRFA20 decreased from 13.35% to 1.01% in the range of 1075–1125°C, while the fast melting of this group occurred at 1075–1100°C, and the absolute value of the water absorption curve slope was 0.40. The fast melting of PRFA40 occurred in the temperature range of 1100–1125°C, and the absolute value of the water absorption curve slope in this region was 0.27. Notably, the spherical bodies obtained in this work were porous structures composed of fine particles with large numbers of open pores on their surfaces, and the internal pores of the spherical bodies were connected to each other, thus increasing the absorption space. With the production of the melt during sintering, the liquid phase gradually filled and covered the pores and simultaneously converted the open pores on the surface into closed pores, thereby shrinking and closing the absorption space and reducing the water absorption rate. Therefore, the observed decrease in water absorption rate can reflect the amount of melt produced during the sintering process and its fluidity.
For the five groups of samples, the calculated SiO$_2$ /∑flux values were $I_{DCPR} = 1.72$, $I_{PRFA20} = 1.95$, $I_{PRFA40} = 2.23$, $I_{PRS20} = 1.97$, and $I_{PRS40} = 2.25$, and the corresponding (SiO$_2$+ Al$_2$O$_3$)/∑flux values were $R_{DCPR} = 2.14$, $R_{PRFA20} = 2.60$, $R_{PRFA40} = 3.15$, $R_{PRS20} = 2.50$, and $R_{PRS40} = 2.90$. Thus, (SiO$_2$+ Al$_2$O$_3$)/∑fluxing was inversely proportional to absolute value of the water absorption curve slope. The higher was the (SiO$_2$+ Al$_2$O$_3$)/∑flux ratio, the higher was the sintering temperature required for rapid melting, that is, the temperature required to produce a melt. Moreover, during the fast-melting stage, the melt viscosity increased and its fluidity decreased.

### 3.3. Crystal transformation

JADE6.0 software was used to analyze the XRD patterns of the sintered LWAs and spherical bodies to be sintered (Figure 3). Figure 3(a) shows the XRD patterns of DCPR, PRFA40, and PRS40 with different compositions sintered at 1100°C. DCPR-1100-10 mainly consisted of barite crystals (BaSO$_4$) with small amounts of barium feldspar (BaAl$_2$Si$_2$O$_8$) and potassium feldspar crystals (K$_2$Al$_2$Si$_2$O$_8$). The PRFA40-1100-10 and PRS40-1100-10 spectra contain the celsian and anorthite peaks. The barite peak at 2θ = 43.2° was significantly reduced, while the other barite peaks almost disappeared. In addition, the characteristic SiO$_2$ peak at 2θ = 22° revealed that after varying the contents of Si, Al, and other metal elements, a certain amount of the SiO$_2$ phase remained in the sample after sintering. Furthermore, CaSiO$_3$ peaks appeared at 2θ = 26° and 2θ = 29°.

Figure 3(b,c) displays the XRD patterns of the PRFA40 and PRS40 LWAs sintered at 1050, 1100, and 1150°C for 10 min, which reflect the differences between the crystals formed at different sintering temperatures. After sintering, these crystals were restructured, and the original crystals such as quartz and unstable calcite were transformed into those with more complex structures, higher strengths, and more stable chemical properties, such as celsian and anorthite. At the same time, a large amount of BaSO$_4$ also decomposed at high temperatures. In this process, Ba atoms penetrated the crystal structure and formed complex aluminosilicate crystals containing Al, Si, and O atoms (their locations were similar to those of the Ca atoms in anorthite crystals [54]).

After comparing Figure 3(b,c), it was found that at a sintering temperature of 1150°C, a significant difference was observed between the XRD spectral lines of PRFA40 and PRS40. Compared with the XRD pattern of PRS40-1100-10, the peak heights of PRS40-1150-10 and their number were reduced, indicating that the crystallinity and grain size of the sample changed considerably. Unlike PRS40-1150-10, no significant changes were observed for the PRFA40-1150-10 sample.

### 3.4. Microscopic morphology and crystal structure

Figure 4 displays the morphologies of LWAs observed by scanning electron microscopy (SEM). It shows that as the sintering temperature increased, the sample surface became smoother and flatter. This occurred because at higher temperatures, a larger amount of the liquid phase was produced, which filled the pores between particles and formed a glass phase with a smooth and flat surface after cooling. In this process, the glass-phase structure produced by cooling the melt coated the crystal particles, forming a structure similar to that of concrete. Owing to the presence of the glass phase, the crystal surface was in close contact with the glass phase, which increased the force-bearing area, thereby avoiding stress concentration, reducing the stress per unit area of the crystal surface, and increasing the overall strength of the material. In the temperature region of 1050–1150°C, the PRS40 surface was always flatter than that of the PRFA40 surface sintered at the same temperature because PRS40 produced a larger melt amount and exhibited lower viscosity, higher fluidity, and larger volume of the glass phase.

Figure 5(a) shows the transmission electron microscopy (TEM) image of the PRFA40-1100-10 sample and results of TEM scanning of crystal particles (b) in this area by EDS. The distributions of Si, Al, and Ca

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**Figure 3.** XRD patterns of sintered ceramic aggregates. DCPR, PRFA40, and PRS40 sintered at 1100°C. (b) PRFA40. (c) PRS40.
elements in the studied area were nearly identical, and their positions are designated by the bright field in Figure 5(a). The contents of these elements at the position depicted by the dark field were relatively small, while S and Ba were predominant in the studied area. These results suggest that the dark field area corresponded to BaSO₄ species, while the bright field area was mainly composed of anorthite crystals or the glass phase containing Si, Al, and Ca atoms. After comparing the distributions of Ba and S atoms, a slight difference between them was detected: area B had a higher concentration of Ba atoms, while its content of S atoms was very small. A high-resolution image of this area is presented in Figure 5(b).

The apparent grid structure formed by the aluminosilicate crystal lattice is observed in area B in Figure 5(b). This structure is regular and stable, and its fringes are parallel to each other with equal spacings. The fringes extended to area A, while the direction of the lattice stripes did not change. In area A, owing to the influence of BaSO₄ on the electron beam, regular and parallel wave-shaped fringes with a wavelength of

\[ \lambda = \frac{22.16 \text{ nm}}{2} \]

were observed. A high-resolution image of this area is presented in Figure 5(b).
1.46 nm were generated in the resulting image in a direction that was not parallel to the fringes in area A. The main elements in the bright field area C were Si, Al, O and Ca; the predominant crystal chemical formula in this area was \( \text{CaAl}_2\text{Si}_2\text{O}_6 \), and the main chemical formula of the crystal phase in area B was \( \text{BaAl}_2\text{Si}_2\text{O}_6 \). Although the chemical formulas in the two regions were different, the grid structure demonstrated good continuity and was highly consistent with the crystal structure in area B, indicating that the crystal phases in the two regions actually belong to the same crystal grain. The fringe spacings in areas B and C were the same (0.34 nm) as the fringes mainly depended on the Si-Al-O structure but did not include metal cations. A part of area C (inside the red circle) was a glass phase amorphous structure produced by the atoms that failed to rearrange to form a crystal structure during the cooling of the liquid phase; as a result, no fringes were observed in this region. Nearby, lattice fringes with a lattice spacing of 0.30 nm and angle of 22.16° were detected, which indicated that the liquid-phase fluidity was limited owing to the uneven elemental distributions, leading to the formation of another crystal phase.

### 3.5. LWA density improvement

Among the studied samples, the \( (\text{SiO}_2 + \text{Al}_2\text{O}_3) / \Sigma \text{flux} \) value of PRFA40 equal to RPRFA40 = 3.15 was the closest one to the criterium established by Gennaro [32]. In general, LWAs should possess low weights combined with relatively high strengths. When the sintering temperature exceeded 1100°C, as the crystal grains melted, the liquid phase filled the pores in the final product, resulting in the collapse of the ceramics structure and volume shrinkage. As a result, the particle density increased.

Therefore, in this study, SiC was applied as an expansion agent, and the sintering time was extended to 20 min. \( \text{CO}_2 \) and \( \text{CO} \) were released during SiC oxidation at temperatures over 1000°C via the following reactions [39,55]:

\[
2\text{SiC} + 3\text{O}_2 \rightarrow 2\text{SiO}_2 + 2\text{CO} \\
\text{SiC} + 2\text{O}_2 \rightarrow \text{SiO}_2 + \text{CO}_2
\]

Meanwhile, \( \text{Fe}_2\text{O}_3 \) serving as an oxygen source also produced \( \text{CO} \) and \( \text{CO}_2 \) gases during its reaction with SiC [56,57]:

\[
\text{SiC} + 3\text{Fe}_2\text{O}_3 \rightarrow \text{SiO}_2 + 6\text{FeO} + \text{CO} \\
\text{SiC} + 4\text{Fe}_2\text{O}_3 \rightarrow \text{SiO}_2 + 8\text{FeO} + \text{CO}_2
\]

In this process, the liquid phase in ceramic aggregates blocked most pores and exhibited sufficiently high viscosity to prevent the generated gases from escaping. Owing to the continuous gas generation and thermal expansion, the gas accumulated in the liquid phase to produce a high pressure. As the pressure continued to increase and exceeded the surface tension of the liquid phase on the bubble boundary, the gas-filled pores expanded, as shown in Figure 7(b,c). This increase in the internal pore volume of ceramic aggregates increased their overall volume (Figure 7(a)).

In summary, the generated gas expanded LWAs and thus reduced their density. At a sintering temperature of 1100°C, the particle densities of PRFA40-SC2.5 and PRFA40-SC5.0 decreased to 1626 and 1436 kg/m\(^3\), respectively, while the density of PRFA40 was 2088 kg/m\(^3\). With the further increase in the sintering
temperature to 1125°C, the particle densities of PRFA40-SC2.5 and PRFA40-SC5.0 decreased to 1375 and 956 kg/m³, respectively (Figure 6).

As the temperature further increased, SiC expander chemically reacted with Fe₂O₃:

A Mercury porosimetry analyzer was used to measure the distribution of LWA pore sizes smaller than 200 μm (Figure 8). First, we determined the pore size distribution of LWAs with different formulations sintered at 1100°C. The DCPR LWA structure collapsed leaving intact only the pores with sizes less than 1 μm, which accounted for 89.09% of the total pore volume. The pore sizes of PRFA40-1100-20 and PRFA40-SC2.5–1100-20 varied between 10 and 25 μm, accounting for 66.61% and 59.51% of the total pore volume, respectively. However, in the size range of 25–80 μm, the number of pores in PRFA40-SC2.5–1100-20 (12.71%) was significantly higher more than those in PRFA40-1100-20 (5.31%). In PRFA40-SC5.0–1100-20, the number of pores with sizes smaller than 25 μm (40.72%) apparently decreased, and the pore sizes mainly ranged between 0 and 25 μm, accounting for 59.25% of the total pore volume, and the fraction of large pores with diameters over 150 μm was relatively high.

For comparison, in the PRFA40-SC2.5–1050-20 and PRFA40-SC2.5–1075-20 samples, the fraction of the large pores with diameters over 120 μm decreased from 14.37% to 10.28% (these large pores existed previously in the green bodies). The pores were retained owing to the irregular particle shapes (because the material was sintered at 1050°C, its LWAs contained a very small melt amount and their fluidity was low). As a result, the size distribution range of small pores in

![Figure 7. Illustration of the PRFA40-SC2.5 LWA foaming process.](image-url)
4. Conclusion

The sintering of LWAs is divided into three stages: melting, restructuring and expansion. At the melting stage, crystals are converted into a liquid phase, and the original pores shrink. During the restructuring stage, after the addition of CFA and SHA to adjust the Si–Al–(Ca+Ba) ratio, Al atoms replace some Si atoms in the original crystal lattice in the form of four ligands, forming aluminosilicate crystals with a more complex and stable structure, which can effectively increase the compressive strength of LWAs. According to TEM observations, the sintering process promotes the diffusion of Ba atoms from BaSO<sub>4</sub> into the aluminosilicate structure to form the celsian phase. BaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub> and CaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub> species co-exist in the same crystal grains, and their crystal structures are highly consistent. In addition to the crystal strength, another factor affecting the compressive strength of LWAs is the content of the glass phase, which forms a concrete-like structure by bonding crystal grains. As the sintering temperature increases, the compressive strength of LWAs increases to the maximum value and then gradually decreases with an increase in the fraction of the glass phase. At the expansion stage, with the addition of SiC serving as an expansion agent, the produced CO<sub>2</sub> gas is intercepted by the liquid melt with sufficiently high viscosity, thereby generating a porous structure, expanding LWAs, and reducing the particle density. As a result, LWAs with high strength and low density were successfully prepared.

Disclosure statement

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