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A multifunctional ZrC porous ceramic fabricated via a direct foaming method with load-bearing, thermal insulation, and electromagnetic wave absorption properties

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Abstract

To meet the growing demand for multifunctional integrated materials with enhanced thermal insulation, electromagnetic wave absorption, and load-bearing capabilities, a porous ZrC ceramic was synthesized via a polymer-induced self-foaming method. This approach employed commercial ZrCl₄ and furfural as precursors, followed by in situ polymerization, carbothermal reduction, and high-temperature sintering to obtain the target material. The resulting porous ZrC ceramic exhibits a unique three-dimensional pore structure composed of interconnected ZrC microspheres, with a porosity of 71.0%. The material demonstrates excellent thermal insulation performance, with a thermal conductivity of 0.254 W·m⁻¹·K⁻¹, along with superior electromagnetic wave absorption capability, achieving a minimum reflection loss (RL_{min}) of -28.87 dB. Furthermore, strong interfacial bonding between the microspheres ensures good mechanical strength, with a compressive strength reaching 23.6 MPa. This polymer-induced self-foaming

method provides an innovative route for designing high-performance, multifunctional porous ceramics.

Keywords

ZrC Porous Ceramic, Electromagnetic Wave Absorption, Thermal Insulation, Mechanical Properties

1 Introduction

During atmospheric reentry, hypersonic vehicles face extreme operating conditions involving the coupled effects of aerodynamic heating, intense electromagnetic radiation, and significant thermo-mechanical coupling loads [1, 2]. This demands that thermal protection materials simultaneously meet multiple functional requirements. On one hand, they must maintain excellent thermal stability and insulation performance at ultra-high temperatures to ensure the safe operation of internal components. On the other hand, they need sufficient mechanical load-bearing capacity to withstand aerodynamic loads at high Mach numbers, while also possessing strong electromagnetic wave absorption properties to achieve radar stealth and electromagnetic compatibility [3, 4]. Conventional thermal protection systems address these challenges using separate components—such as metal/ceramic load-bearing structures, porous ceramics or aerogel insulation layers, and metal-based electromagnetic shielding coatings. However, this approach not only significantly increases system mass but also introduces critical reliability issues such as thermal expansion mismatch, interfacial delamination, and redundant spatial layout due to the presence of multiple heterogeneous interfaces [5-7]. Therefore, developing a multifunctional integrated material system that combines structural load-bearing capability, efficient thermal insulation, and controllable electromagnetic response has become a key technological bottleneck for breakthrough designs in next-generation

hypersonic vehicle thermal protection systems.

Introducing porous structures is an effective approach to reduce material density and thermal conductivity, while also enhancing electromagnetic wave absorption capabilities, as pore interfaces can induce multiple reflections and scattering [8-11]. However, porosity inevitably compromises the mechanical properties of materials. Although the layered porous SiC ceramics prepared by Liu et al. [12] using a foam gel casting method exhibit excellent thermal insulation ($0.109 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$) and infrared stealth performance, their compressive strength is only 0.14 MPa, insufficient for load-bearing applications. Similarly, the SiC nanofiber aerogels synthesized by Song et al. [13] demonstrate outstanding electromagnetic wave absorption ($RL_{\min} = -61.56 \text{ dB}$) and thermal insulation ($0.026 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$), but their strength remains at the kilopascal level, making them unsuitable for structural applications [14, 15]. Existing studies indicate that improving the thermal insulation of porous ceramics typically relies on increasing porosity, which precisely leads to mechanical degradation [16], rendering the synergistic optimization of material properties a highly challenging task.

Ultra-high temperature ceramics (UHTCs), such as ZrC, HfC, and TaC, are considered ideal candidates for thermal protection materials in extreme high-temperature environments due to their melting points above 3000°C , excellent high-temperature strength, and chemical stability [17-19]. Among them, ZrC has attracted considerable attention because of its relatively low density and good thermal shock resistance [20, 21]. However, the high intrinsic thermal conductivity of dense ZrC ceramics limits their direct application as thermal insulation materials. Studies have shown that fabricating ZrC into porous structures can significantly reduce thermal conductivity, enabling it to be lowered to the range of $0.2\text{--}1 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ by adjusting porosity [22]. Furthermore, the electrical conduction loss caused by the three-

dimensional conductive framework in porous ZrC, along with multiple scattering effects induced by pore structures, endows it with certain electromagnetic wave absorption potential [23, 24]. Nevertheless, further research is still needed to simultaneously optimize the thermal insulation and microwave absorption properties of porous ZrC ceramics without significantly compromising their mechanical performance.

In terms of preparation methods, the self-foaming approach has attracted considerable attention due to its simplicity and efficiency [25]. This method directly forms a foam structure by releasing gas from precursors during polymerization, without requiring external foaming agents or templates, enabling one-step fabrication of highly porous ceramics [26-28]. Li et al. successfully synthesized TiC/ZrC porous ceramics with a porosity of 75.2% using metal chlorides and furfural as precursors via the self-foaming method, achieving a thermal conductivity as low as $0.21 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ and a mechanical strength of 26 MPa, demonstrating excellent integrated thermal insulation and mechanical properties [17]. He et al. further introduced ultrasound assistance to fabricate carbon fiber-reinforced high-entropy carbide porous ceramics, achieving outstanding electromagnetic wave absorption performance of -59.25 dB [29]. However, research on the structural-functional integration of ZrC porous ceramics via the self-foaming method remains insufficient, particularly regarding the systematic understanding of how carbon source content regulates microstructure and overall performance. In the polymer precursor route, the stoichiometric ratio between the carbon source (foaming agent) and the metal source directly influences the progress of carbothermal reduction reactions, residual carbon content, and degree of graphitization, thereby significantly affecting the material's phase composition, micro-pore structure, mechanical properties, and dielectric characteristics. Therefore, clarifying the

regulation mechanism of the C/Zr ratio on the microstructure and multifunctional properties of ZrC porous ceramics is crucial for their targeted performance design.

This study employs ZrCl_4 as the zirconium source and furfural as both the carbon source and foaming agent to prepare porous ZrC ceramics via a self-foaming method combined with high-temperature carbothermal reduction. The influence of the C/Zr ratio on the phase composition, microstructure, pore structure, mechanical properties, thermal insulation performance, and electromagnetic wave absorption properties of the material is systematically investigated. The mechanism by which carbon content 调控 affects the porous structure and multifunctional characteristics is revealed, providing experimental support for the structural design and performance optimization of lightweight, load-bearing, thermally insulating, and microwave-absorbing integrated porous ZrC ceramics.

2. Experimental

2.1. Materials

Zirconium tetrachloride (ZrCl_4 , 99.9% purity), furfural (FA, 98% purity), and ethanol ($\text{C}_2\text{H}_5\text{OH}$, 99.9% purity) were all purchased from Aladdin Bio-Chem Technology Co., Ltd. (Shanghai, China). All reagents were used as received without further purification.

2.2. Preparation of ZrC porous ceramic

Weigh 2.8 g of zirconium tetrachloride into a beaker, add 10 mL of anhydrous ethanol, and dissolve thoroughly. Under an ice bath, stir magnetically at 600 rpm for 60 min to obtain an acidic zirconium salt alcohol solution. Using furfural as the carbon source and the zirconium salt alcohol solution as the zirconium source, prepare four precursor mixtures with C/Zr molar ratios of 9:1, 10:1, 11:1, and 12:1, respectively. After magnetic stirring at 600 rpm under an ice bath for 30 min, allow the mixture to stand undisturbed. During this period, furfural in the precursor solution spontaneously

polymerizes and releases gas, forming a porous green body. The amounts of metal and carbon sources added are shown in Table 1.

Table 1 The addition amounts of metal alcoholates and furfuryl alcohol

Sample	ZrCl ₄ n(mol)	ZrCl ₄ m (g)	Furfuryl alcohol n (mol)	Furfuryl alcohol m (g)	Carbon source n (mol)
Z1	0.012	2.8	0.0216	2.12	0.108
Z2	0.012	2.8	0.0240	2.35	0.120
Z3	0.012	2.8	0.0264	2.59	0.132
Z4	0.012	2.8	0.0288	2.83	0.144

After drying the aforementioned porous green body at 60 °C for 12 h, it was pre-sintered under an argon atmosphere at 800 °C for 2 h. The pre-sintered precursor was then subjected to high-temperature carbothermal reduction sintering: protected throughout by argon, heated from room temperature to 1400 °C at a rate of 5 °C/min, followed by further heating to 1600 °C at 2 °C/min, held at this temperature for 120 min, and cooled down with the furnace after completion of the program, ultimately yielding porous ZrC ceramics with different C/Zr ratios. The preparation process is shown in Fig. 1.



Figure 1 Schematic diagram of the preparation process for ZrC porous ce-ramic.

2.3. Characterization methods

The phase composition of the synthesized samples was characterized by X-ray diffraction (XRD; Smart Lab, Rigaku, Japan) using Cu K α radiation ($\lambda = 1.540593 \text{ \AA}$). Morphology was observed via scanning electron microscopy (SEM; Regulus 8100, Hitachi, Japan). Microstructural analysis was performed using transmission electron microscopy (TEM; Themis Z, FEI, USA) equipped with an energy-dispersive X-ray spectroscopy (EDS) system. The degree of graphitization in the porous ceramics was evaluated by laser micro-Raman spectroscopy (DXRxi, Thermo Fisher Scientific, USA). Pore size distribution and porosity were determined by mercury intrusion porosimetry (AutoPore IV 9500, Micromeritics, USA). Dielectric parameters were obtained using a vector network analyzer (Agilent 85071 E, Santa Clara, CA, USA). Thermal conductivity (λ) was measured using a thermal constant analyzer (TPS2200, Hot Disk, Sweden) based on the transient plane source method according to ISO 22007-2.2, enabling rapid determination within seconds. Compressive strength was tested at room temperature using a universal testing machine (UTM 5105, Sans, China) with a crosshead speed of 0.5 mm/s. Infrared thermal images were captured using an infrared thermal imager (TIS75+, FLUKE, USA).

3. Results and discussion

3.1. Microstructural evolution of ZrC porous ceramic

Fig. 2a shows the XRD patterns of porous ZrC ceramics synthesized at different C/Zr ratios. All samples exhibit clear and sharp diffraction peaks at $2\theta = 33.5^\circ, 38.8^\circ, 55.8^\circ, 66.3^\circ$, and 69.8° , corresponding to the (111), (200), (220), (311), and (222) crystal planes of cubic-phase ZrC, respectively, which perfectly match the characteristic peak positions in the standard card. This indicates that pure-phase porous ZrC ceramics were successfully synthesized under high-temperature carbothermal reduction at 1600°C across all C/Zr ratios, with no detectable ZrO_2 impurity phase. As the amount of furfural

added to the precursor (i.e., C/Zr ratio) increases, the characteristic ZrC diffraction peaks remain sharp, with no significant broadening of the peak half-width or notable reduction in peak intensity. This demonstrates that adjusting the C/Zr ratio does not disrupt the crystalline structure of ZrC; the crystal orientation and crystallinity of cubic-phase ZrC remain stable, and carbon primarily exists as free carbon within the ZrC matrix.

Fig. 2b1–b8 shows SEM images of porous ZrC ceramics under different C/Zr ratios, where Fig. 2b1 and 2b5 correspond to sample Z1, Fig. 2b2 and 2b6 to sample Z2, Fig. 2b3 and 2b7 to sample Z3, and Fig. 2b4 and 2b8 to sample Z4. At low magnification, all samples Z1–Z4 exhibit continuous, interconnected three-dimensional porous structures formed by stacked ceramic particles, with uniformly distributed pores and no obvious macroscopic defects. This structure originates from the polycondensation foaming reaction between furfural and zirconium tetrachloride in an ethanol system, followed by the release of large amounts of CO and CO₂ gases during subsequent high-temperature carbothermal reduction [28]. It can be observed that initial skeletal connections among particles are formed via necking effects (Fig. 2b4). As the C/Zr ratio in the precursor increases gradually, at higher magnification, ZrC particles transition from sharp-edged, irregular shapes with uneven sizes (Fig. 2b5) to smooth-surfaced, uniform spherical or near-spherical particles (Fig. 2b8). Simultaneously, as the C/Zr ratio increases, the particle agglomerates become looser with thinner connecting necks, evolving into a state where interparticle contact interfaces significantly expand, sintering neck thickness markedly increases, and the skeletal connections become more robust and dense (Fig. 2b8). This indicates that sufficient carbon source not only ensures complete carbothermal reduction, providing favorable conditions for uniform ZrC grain growth, but also promotes the development of sintering necks between

particles, ultimately optimizing the porous structure and densifying the skeleton. Consequently, the microstructure of the porous ZrC ceramics becomes more regular and stable, laying a solid microstructural foundation for the material's subsequent performance. Fig. 2c displays the elemental distribution of sample Z4, confirming that both carbon and zirconium elements are present throughout the ceramic skeleton, verifying its composition as ZrC.

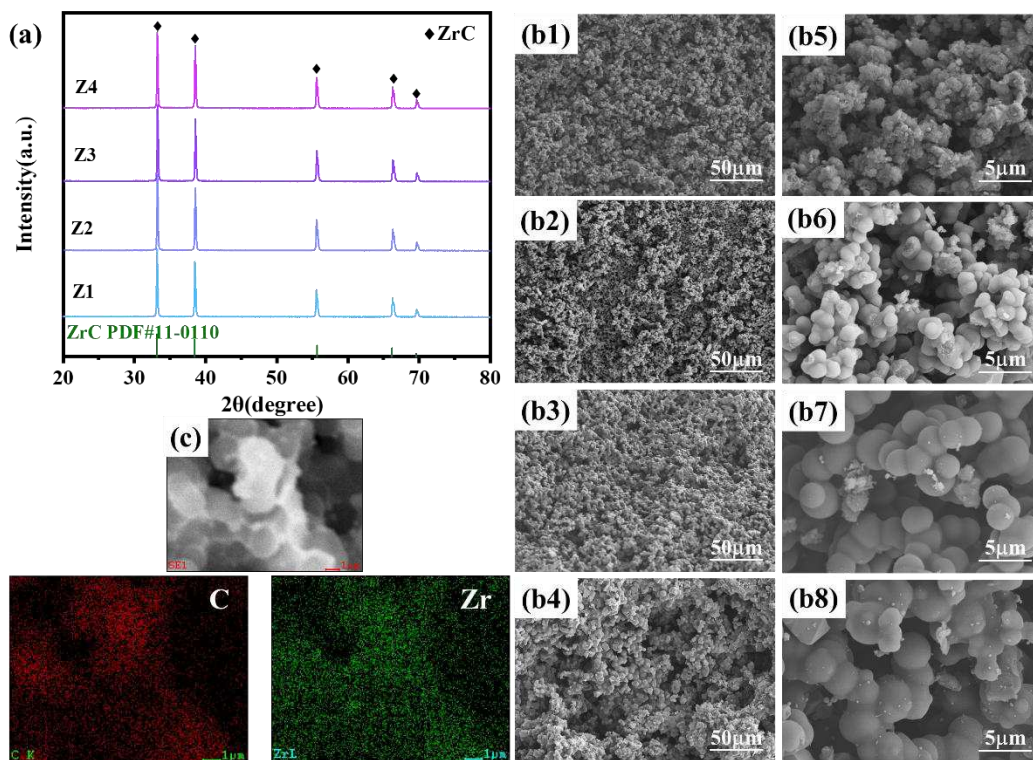


Figure 2 (a) XRD patterns, (b1–b8) SEM images, and (c) EDS spectrum of ZrC porous ceramics at different C/Zr ratios.

Fig. 3a–d shows the Raman spectra of porous ZrC ceramic samples with different C/Zr ratios, along with peak deconvolution analysis. All samples exhibit distinct characteristic peaks near 1350 cm^{-1} and 1580 cm^{-1} , corresponding to the D-peak and G-peak of carbon materials, respectively. The D-peak is associated with disordered or defective carbon vibrational modes, reflecting the presence of defects, edge sites, and amorphous carbon in the carbon lattice, while the G-peak corresponds to the in-plane stretching vibration of sp^2 -hybridized graphitic carbon, serving as a key indicator of

carbon structural orderliness. These results confirm the existence of free carbon phases within the porous ZrC ceramics. By performing peak deconvolution on the Raman spectra, the intensity ratios (I_D/I_G) of the D-peak to the G-peak were quantitatively calculated for each sample, as shown in Fig. 3e. The data reveal a monotonic decrease in I_D/I_G values with increasing C/Zr ratio, dropping gradually from 1.92 in sample Z1 to 1.51 in sample Z4. The I_D/I_G ratio is a critical parameter for characterizing the degree of graphitization in carbon materials [30]. Its reduction indicates that as the C/Zr ratio in the precursor increases, the graphitization level of the free carbon phase within the ZrC matrix significantly improves. The systematic enhancement in carbon structural orderliness and the corresponding decrease in defect concentration suggest that the C/Zr ratio plays a significant role in the evolution of the free carbon structure. An abundant carbon source provides favorable reaction conditions for carbon rearrangement and graphitization, promoting the transformation of amorphous carbon into ordered graphitic carbon, thus laying a structural foundation for subsequent tuning of the material's electromagnetic and mechanical properties.

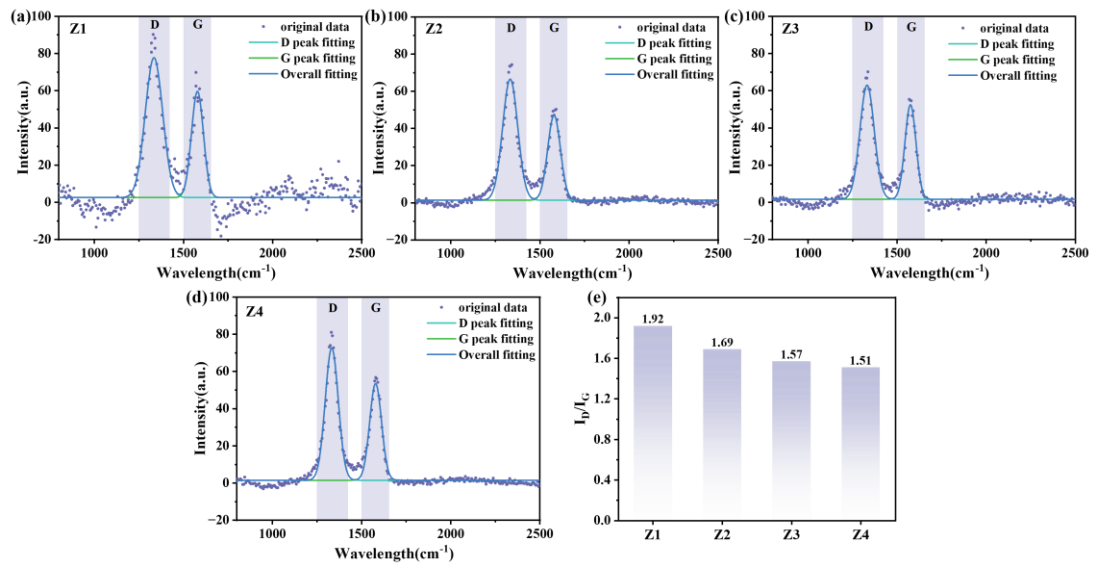


Figure 3 (a–d) Raman spectra and (e) I_D/I_G values of porous ZrC ceramic samples at different C/Zr ratios.

Fig. 4a–c shows the pore size distribution curves of ZrC porous ceramic samples at different C/Zr ratios. It can be observed that all samples exhibit pore sizes concentrated within the micrometer range, displaying a unimodal distribution, indicating good uniformity in the pore structure. As the C/Zr ratio increases, the pore size distribution broadens systematically: the pore size range for sample Z1 is 0.6–3 μm , expands to 0.8–4.4 μm for Z2, further extends to 0.6–5 μm for Z3, and reaches 0.4–6 μm for Z4, while the peak position of the pore size shifts toward larger dimensions. These results confirm that adjusting the C/Zr ratio enables effective and controllable fabrication of the pore structure in ZrC porous ceramics; increasing the C/Zr ratio promotes the formation of larger pores, providing a structural basis for optimizing the material's thermal insulation performance. Fig. 4e presents the porosity and density of ZrC porous ceramics at different C/Zr ratios. It is evident that as the carbon source content increases from Z1 to Z4, the porosity rises significantly from 54.6% to 71.0%, while the corresponding bulk density gradually decreases from 0.79 g/cm^3 to 0.64 g/cm^3 . This is because furfural acts not only as a carbon source but also functions as a foaming agent under acidic conditions [28]. With increased furfural content, more gaseous byproducts are released during pyrolysis, generating additional pores within the ceramic matrix, resulting in a more porous and less dense material. Additionally, since carbon itself has a low density, excessive addition of carbon further reduces the overall bulk density of the material.

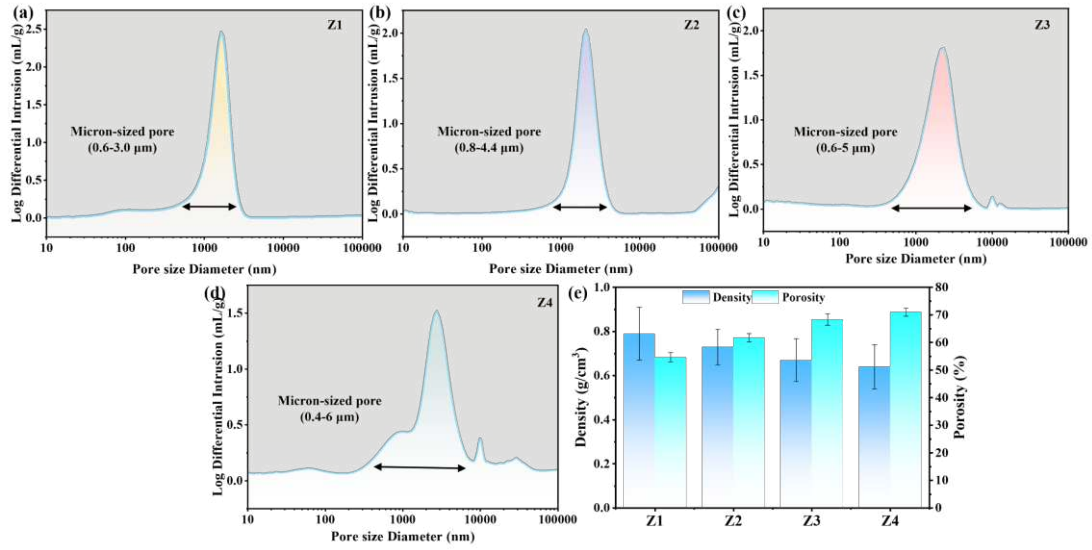


Figure 4 (a-d) Pore size distribution curves of ZrC porous ceramic samples at different C/Zr ratios, and (e) changes in porosity and density.

3.2. Electromagnetic wave absorption properties of porous ceramic

The system evaluated the electromagnetic wave absorption performance of porous ZrC ceramic samples at different C/Zr ratios. The electromagnetic wave dissipation capability can be quantified by reflection loss (RL), which is calculated using equations (1) and (2):

$$Z_{in} = \sqrt{\frac{\mu_r}{\epsilon_r}} \tanh \left[j \frac{2\pi f d}{c} \sqrt{\mu_r \epsilon_r} \right] \quad (1)$$

$$RL = 20 \log_{10} \left| \frac{Z_{in} - 1}{Z_{in} + 1} \right| \quad (2)$$

Here, Z_{in} represents the input impedance of the absorber; ϵ_r and μ_r denote the relative complex permittivity and permeability, respectively; f is the frequency of the incident electromagnetic wave; c is the speed of light in vacuum; and d is the sample thickness. The lower the RL value, the better the electromagnetic wave absorption performance. Fig. 5a–5c show the real part (ϵ'), imaginary part (ϵ'') (Fig. 5b), and dielectric loss tangent ($\tan \delta\epsilon$) of ZrC porous ceramic samples at different C/Zr ratios. Across the 2–18 GHz frequency range, both ϵ' and ϵ'' of all samples exhibit an overall decreasing

trend with increasing frequency, consistent with typical dispersion characteristics attributable to dipolar polarization. Under alternating electromagnetic fields, dipoles reorient in response to changes in field direction. However, as frequency increases, the reorientation of dipoles lags behind the rapid field variations, resulting in weakened polarization response and thus a reduction in dielectric constant with rising frequency. As the C/Zr ratio increases, both the real and imaginary parts of the complex permittivity of the ZrC porous ceramics show varying degrees of overall decrease. $\tan \delta\epsilon$, as the key parameter characterizing dielectric loss capability, displays weak resonance peaks along with linear segments across the entire frequency band for all four samples, indicating the presence of both polarization loss and conduction loss [31]. Fig. 5d and 5e present the attenuation constant (α) and impedance matching ($|Z_{in}/Z_0|$) of the four ZrC porous ceramic samples. It can be observed that α significantly increases throughout the entire frequency band. Samples Z1 and Z2, possessing higher dielectric loss capabilities, exhibit the highest α values across the tested frequency range; however, their poor impedance matching over the full band leads to suboptimal electromagnetic wave absorption performance. In contrast, sample Z4 demonstrates an impedance matching value close to 1 at specific frequencies, effectively improving the material's impedance matching characteristics and allowing electromagnetic waves to penetrate deeply into the material rather than being reflected at the surface. The combination of suitable $|Z_{in}/Z_0|$ and high α ensures efficient absorption and dissipation of electromagnetic waves.

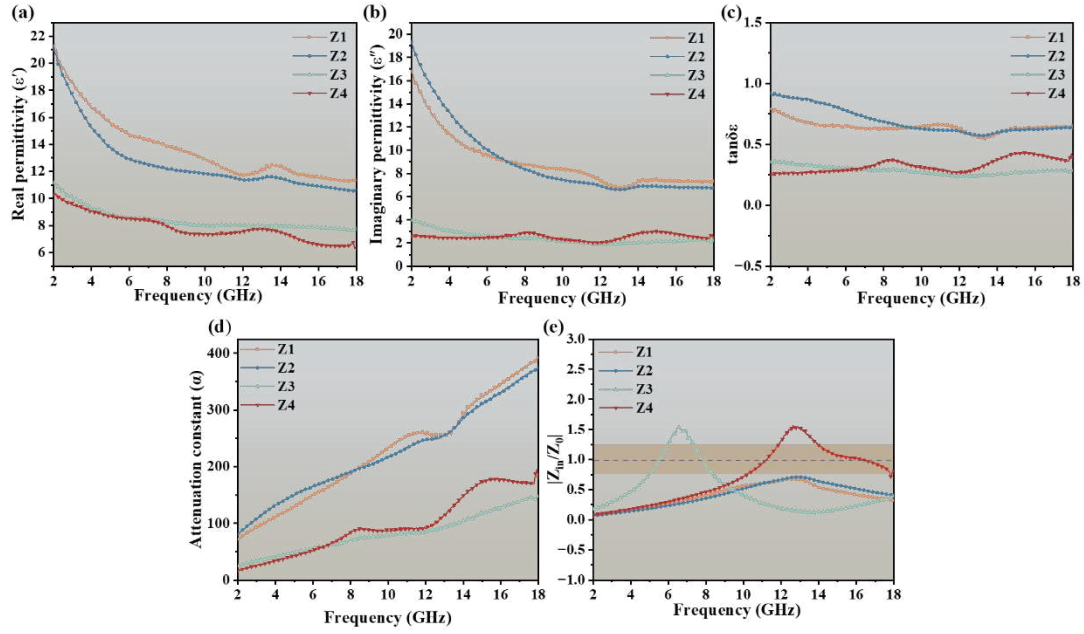


Figure 5 (a) Real part, (b) imaginary part, (c) shear loss, (d) attenuation constant, and (e) impedance matching of the dielectric constant for samples at different C/Zr ratios.

Fig. 6 shows the electromagnetic wave absorption characteristics of ZrC porous ceramics with different C/Zr ratios. Generally, a material is considered to have effective absorption when its reflection loss reaches -10 dB, as this corresponds to the attenuation of 90% of incident electromagnetic waves; the corresponding frequency range is referred to as the effective absorption bandwidth (EAB) [32]. When the reflection loss reaches -20 dB, 99% of the electromagnetic waves are absorbed, and at -30 dB, 99.9% are absorbed. A comparative analysis between the three-dimensional surface plots (Fig. 6a1, 6b1, 6c1, and 6d1) and two-dimensional mapping plots (Fig. 6a2, 6b2, 6c2, and 6d2) reveals that increasing the C/Zr ratio positively enhances the microwave absorption performance. For sample Z1, the minimum reflection loss (RLmin) is only -13.47 dB, corresponding to an effective absorption bandwidth of 2.2 GHz, with an optimal thickness of 1.65 mm. As the C/Zr ratio increases progressively to Z2 and Z3, RLmin decreases to -13.92 dB and -15.70 dB, respectively, while the effective absorption bandwidth expands simultaneously to 3.4 GHz and 1.7 GHz.

Sample Z4 achieves a minimum reflection loss of -28.87 dB and a maximum effective absorption bandwidth of 5.1 GHz at a thickness of 1.96 mm, demonstrating excellent microwave absorption performance characterized by "thin thickness, wide bandwidth, and strong absorption". Fig. 6a3–d3 display the two-dimensional reflection loss and quarter-wavelength matching for ZrC porous ceramics with various C/Zr ratios and different thicknesses. The reflection loss peaks of all samples align closely with the theoretical quarter-wavelength prediction curves, confirming that the electromagnetic wave absorption in ZrC porous ceramics follows the quarter-wave interference cancellation mechanism. With increasing C/Zr ratio, the quarter-wavelength matching curve shifts upward overall, resulting in greater matching thickness at the same frequency, deeper reflection loss peaks, and significantly broader effective absorption bandwidths. Ultimately, sample Z4 achieves a minimum reflection loss of -28.87 dB and a maximum effective absorption bandwidth of 5.05 GHz at a thickness of 1.96 mm, realizing a synergistic optimization of absorption strength, matching thickness, and effective bandwidth.

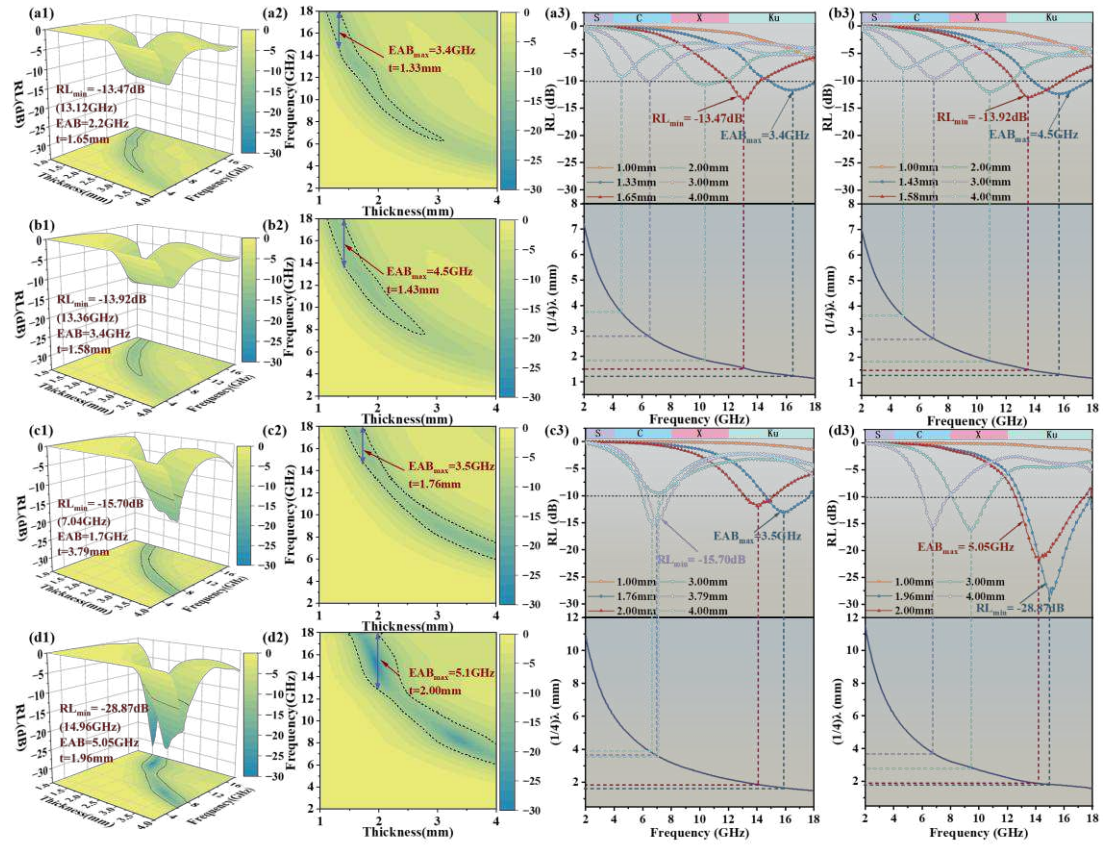


Figure 6 Two-dimensional reflection loss and 1/4 wavelength of ZrC porous ceramics with different thicknesses at various C/Zr ratios: (a) Z1, (b) Z2, (c) Z3, (d) Z4.

Fig. 7 shows the Cole-Cole plots of ZrC porous ceramic samples at different C/Zr ratios. The Cole-Cole plot is used to reveal the polarization relaxation behavior of materials. As seen in the figure, the Cole-Cole curves of samples with low C/Zr ratios mostly exhibit linear segments with only a few polarization semicircles, indicating that electromagnetic waves primarily experience conduction loss through the porous skeleton (Fig. 7a, b). With increasing C/Zr ratio, multiple polarization semicircles become clearly visible in the Cole-Cole plots (Fig. 7c), confirming the presence of multiple Debye-type polarization relaxation processes in ZrC porous ceramics. These polarization relaxation processes are attributed to dipolar polarization caused by residual carbon defects introduced by the elevated C/Zr ratio. At high C/Zr ratios, the curve of sample Z4 displays several complete semicircles, suggesting a richer

polarization relaxation process, where polarization loss plays a dominant role in electromagnetic wave energy attenuation.

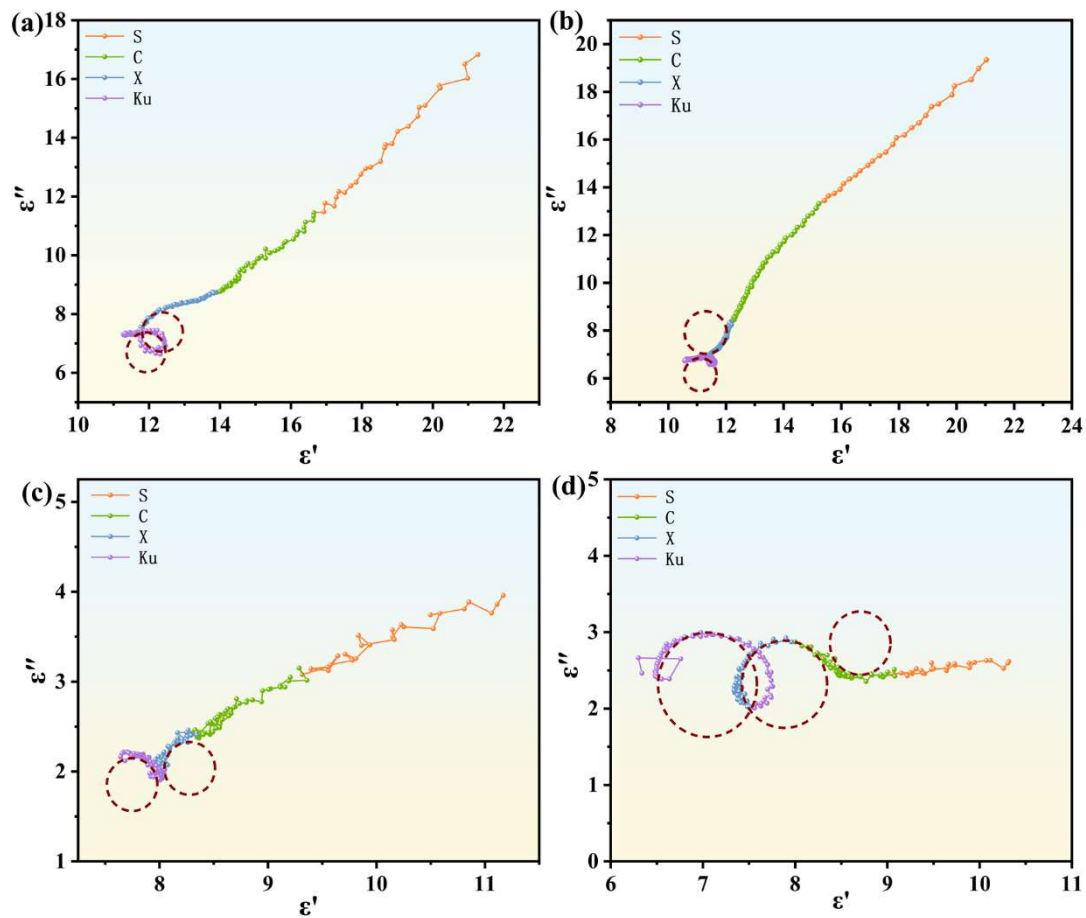


Figure 7 Cole-Cole plots of ZrC porous ceramics at different C/Zr ratios: (a) Z1, (b) Z2, (c) Z3, (d) Z4.

Based on the electromagnetic wave absorption mechanism via dielectric loss, a quantitative analysis of the contributions of conductive and polarization losses in Z4 is conducted. Fig. 8 shows the proportion of conductive and polarization losses in the Z4 sample. The results indicate that conductive loss dominates in the low-frequency range of 2–4.4 GHz and gradually decreases with increasing frequency. Polarization loss exhibits multi-peak characteristics in the frequency bands of 4.4–11.9 GHz, 11.9–12.9 GHz, and 12.9–18 GHz, becoming the primary loss source in the medium- and high-frequency ranges. Increasing the C/Zr ratio enhances conductive loss through higher

carbon content, while also strengthening polarization relaxation by increasing defect concentration. This leads to a synergistic complementarity between conductive and polarization losses across the entire frequency band, providing a loss mechanism foundation for wideband and efficient microwave absorption in the material.

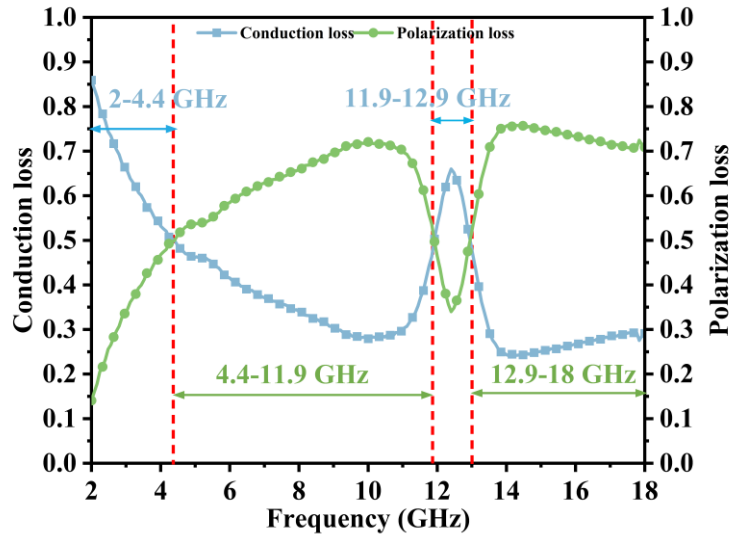


Figure 8 Proportion of conductive loss and polarization loss in the Z4 sample.

To evaluate the actual electromagnetic wave scattering intensity of porous ZrC ceramics under radar radiation, radar cross-section (RCS) simulations were conducted using CST Studio Suite 2025 software. The simulation model adopted a typical two-layer structure, with a perfect electric conductor (PEC) substrate as the base and a top layer of porous ZrC ceramic as the absorption layer. As shown in Fig. 9a, the planar dimensions of the model are $100 \text{ mm} \times 100 \text{ mm}$, with an absorption layer thickness of 3.0 mm and a PEC substrate thickness of 2.0 mm, and the testing frequency was set at 14.96 GHz. As illustrated in Fig. 9b, the bare PEC plate exhibits the strongest scattering signal. After coating with porous ZrC ceramics, Fig. 9b1–b4 show the reflected beam signals for samples Z1 to Z4. It is evident that introducing porous ZrC ceramics significantly suppresses the strong specular reflection from the PEC substrate. With increasing C/Zr ratio, the material's ability to diffuse directional radar wave reflections enhances,

leading to continuous reduction in main lobe intensity and significant improvement in RCS attenuation performance. Sample Z4 demonstrates the best wide-angle RCS suppression capability. Fig. 9d presents a comparison of RCS curves across the full angular range. The pure PEC baseline shows high RCS values, while all porous ZrC ceramic samples exhibit significantly lower two-dimensional RCS curves than the PEC reference, directly confirming the effectiveness of porous ZrC ceramics in suppressing directional radar wave reflections. Further analysis reveals a clear gradient effect of the C/Zr ratio on RCS attenuation performance. Sample Z1 shows limited RCS reduction, whereas the attenuation effect gradually increases for samples Z2 and Z3. Sample Z4 achieves the lowest RCS values across the entire scattering angle range from -90° to 90° , particularly demonstrating excellent wide-angle stealth performance, with RCS values below $-10 \text{ dB}\cdot\text{m}^2$ over the broad angular regions of $-90^\circ < \theta < -10^\circ$ and $10^\circ < \theta < 90^\circ$. Fig. 9e displays the reduction in radar scattering cross-section. It can be observed that sample Z4 exhibits significant echo attenuation at multiple detection angles, reaching maximum attenuation at $\theta = 0^\circ$ (normal incidence), indicating that the material not only dissipates incident electromagnetic energy through dielectric loss but also utilizes its porous microstructure and carbon phase distribution to alter the propagation path of electromagnetic waves, achieving efficient scattering attenuation. Combining the three-dimensional beam patterns and two-dimensional RCS results, it is evident that increasing the C/Zr ratio optimizes the material's microstructure and electromagnetic properties, enabling sample Z4 to achieve highly effective and wide-angle RCS attenuation while maintaining an ultra-thin thickness. In summary, porous ZrC ceramics effectively suppress electromagnetic wave scattering and reflection from PEC surfaces, making them suitable for practical applications in microwave absorption.

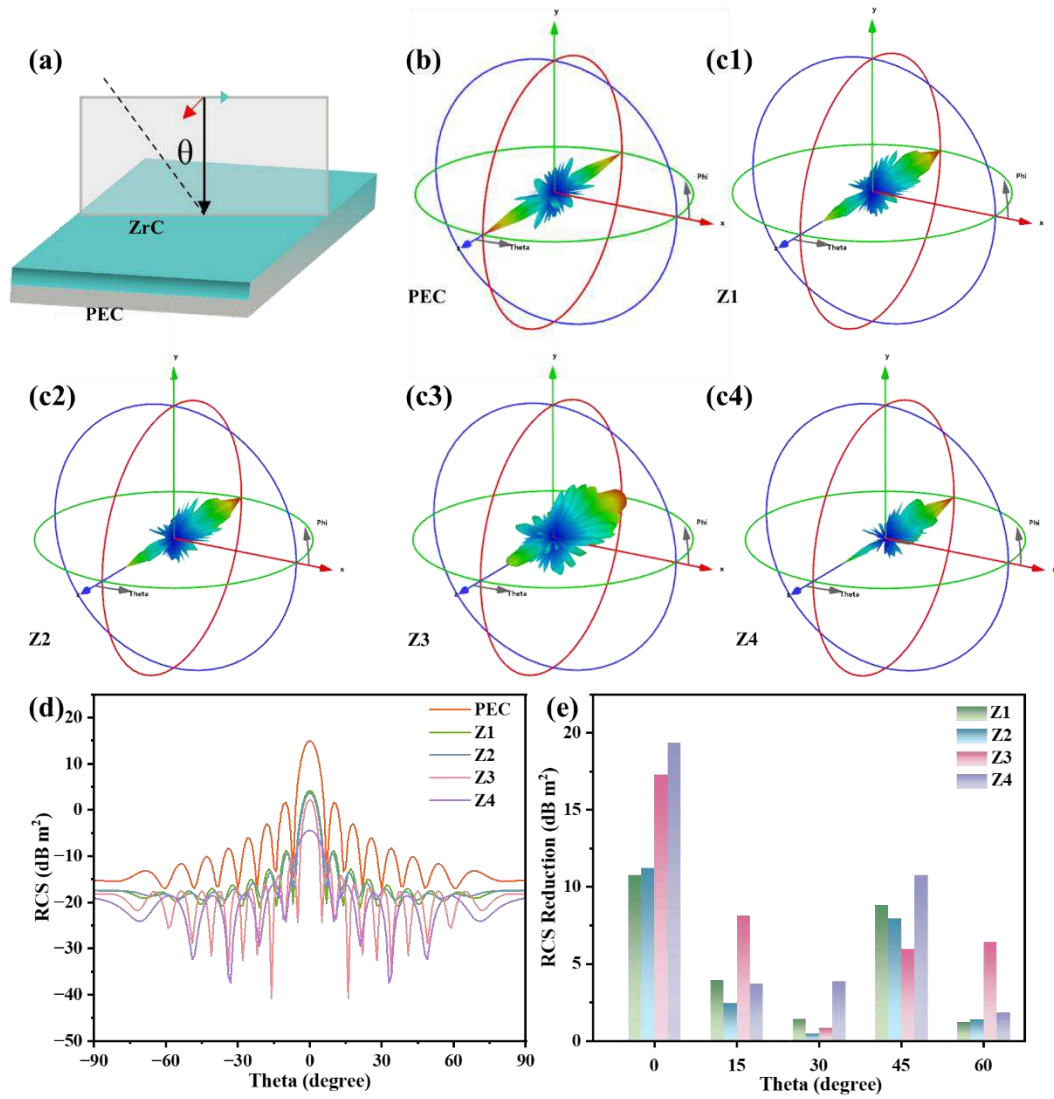


Figure 9 (a) Simulation model, (b) PEC, (c1)-(c4) CST simulation results for Z1-Z4, (d) Simulated RCS curves of PEC and Z1-Z4 at scattering angles from -90° to 90° , (e) RCS reduction values for Z1-Z4.

Fig. 10 illustrates the electromagnetic wave absorption mechanism of porous ZrC ceramics. Incident electromagnetic waves experience energy attenuation through multiple dissipation pathways within the porous ZrC ceramic, with its microwave absorption performance determined synergistically by conduction loss, multiple reflection and scattering, and polarization loss. The three-dimensionally interconnected conductive network provides continuous pathways for electron migration, generating significant conduction loss under an applied alternating electromagnetic field, thereby

converting electromagnetic energy into thermal energy dissipation. The hierarchical porous structure offers abundant interfaces for reflection and scattering, effectively extending the propagation path of electromagnetic waves inside the material and enhancing energy dissipation efficiency. Meanwhile, dipoles induced by carbon defects undergo polarization relaxation under external fields, resulting in substantial polarization loss that further dissipates electromagnetic wave energy. By tuning the C/Zr ratio, the conductive network, pore structure, and polarization behavior are optimized, simultaneously enhancing all loss mechanisms and ultimately enabling the porous ZrC ceramic to exhibit excellent electromagnetic wave absorption performance.

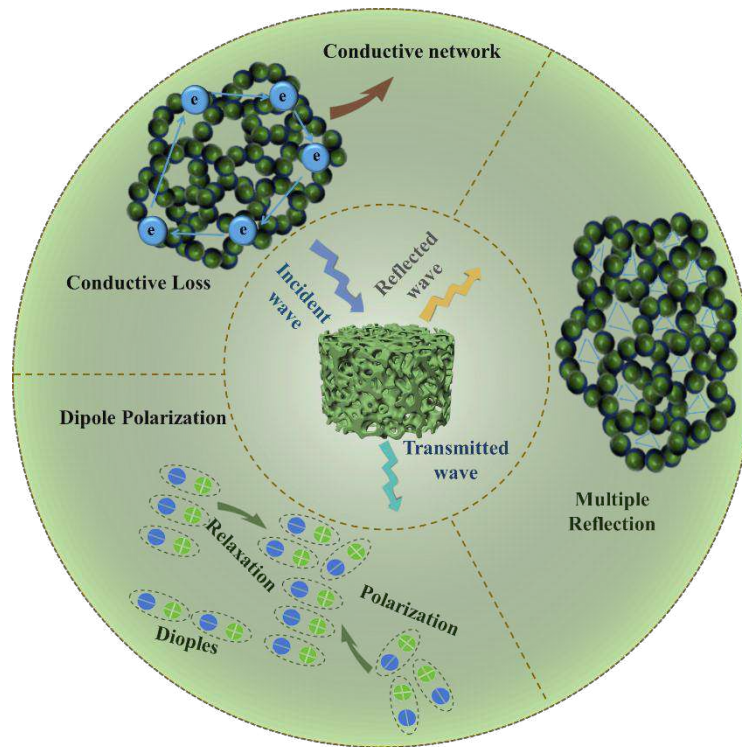


Figure 10 Electromagnetic wave absorption mechanism of porous ZrC ceramics

3.3. Mechanical and thermal insulation properties of ZrC porous ceramic

Fig. 11a and 11b show the stress-strain curves and corresponding compressive strengths of porous ZrC ceramics at different C/Zr ratios. The stress-strain curves all exhibit typical compression behavior characteristic of porous ceramics: during the elastic stage, stress increases linearly with strain; upon reaching yield strength, the

material enters a plastic deformation stage, where stress fluctuates slightly before stabilizing. As the C/Zr ratio increases, the compressive strength of the samples shows a significant stepwise improvement. The compressive strength of sample Z1 is 8.3 MPa, which increases slightly to 15.9 MPa for Z2, further rises to 22.8 MPa for Z3, and reaches a maximum of 23.6 MPa for Z4, representing an 184% increase compared to Z1. During compression, the structural evolution of the porous ceramic is illustrated in Fig. 11c. Initially, the spherical ceramic skeleton undergoes elastic deformation. Upon reaching the elastic limit, inter-particle fractures occur between the spherical grains, leading to irreversible collapse of the three-dimensional network framework. Ultimately, the complete collapse of the internal skeletal structure results in material failure, while compressive stress gradually stabilizes during the final densification stage. This mechanical performance evolution is closely related to the microstructure, porosity, and density changes of the material. Increasing the C/Zr ratio promotes grain growth and sintering densification of ZrC, thereby enhancing the bonding strength between grains. Thus, by tailoring the pore structure, the material maintains both excellent microwave absorption properties and sufficient mechanical load-bearing capacity, meeting the requirements for integrated microwave absorption and structural applications.

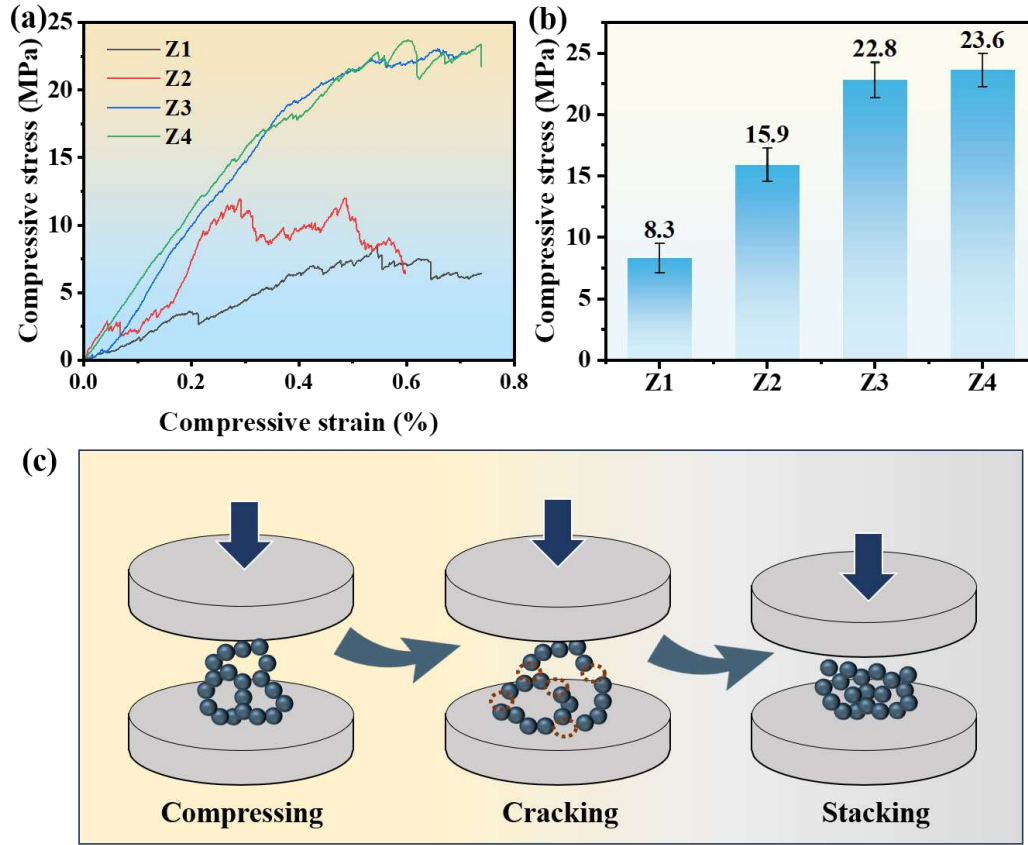


Figure 11 (a) Stress-strain curves, (b) compressive strength, and (c) schematic illustration of structural evolution during compression for ZrC porous ceramics with different C/Zr ratios.

The actual thermal insulation performance of ZrC porous ceramics was evaluated by heating at 300 °C for 10 minutes, as shown in Fig. 12. Fig. 12a presents the infrared thermal images of the ZrC porous ceramics during heating. Under identical heating conditions, the surface temperature at thermal equilibrium systematically decreased from sample Z1 to Z4. The highest surface temperature reached by Z1 was 111.7 °C, while that of Z4 was as low as 99.5 °C, resulting in a temperature difference of 12.2 °C. This trend corresponds precisely with the increasing porosity observed with rising C/Zr ratios (Fig. 4). All samples exhibited a typical radial heat diffusion pattern, characterized by higher temperatures at the center and lower temperatures at the edges. Notably, samples Z3 and Z4 not only had lower overall temperature levels but also

demonstrated significantly improved temperature field uniformity compared to Z1 and Z2. This indicates that high-porosity materials not only suppress solid-state heat conduction through increased pore volume, but their more developed interconnected open pore structures also effectively inhibit potential convective heat transfer via gas, allowing heat to pass primarily through radiation and limited gaseous conduction. As a result, superior and more uniform thermal insulation is achieved. By statistically analyzing the surface temperatures and fitting curves, temperature variation profiles on the sample surfaces under different heating times were obtained, as shown in Fig. 12b. All samples underwent an initial rapid heating phase followed by stabilization; however, Z4 showed the lowest heating rate, which can be clearly observed by comparing the slopes of the temperature change curves. The measured thermal conductivity values of the four samples are presented in Fig. 12c, showing a decreasing trend with increasing C/Zr ratio. The thermal conductivity of Z4 dropped as low as $0.254 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$, indicating excellent thermal insulation performance. The low thermal conductivity originates from the hierarchical pore structure of the ZrC porous ceramics, where stagnant air within pores has extremely low thermal conductivity, effectively blocking phonon and photon heat transfer pathways. Furthermore, the enhanced porosity and larger pore sizes resulting from increased C/Zr ratios further strengthen the thermal barrier effect, enabling the material to achieve the low thermal conductivity required for ultra-high-temperature thermal protection while maintaining outstanding microwave absorption properties. In summary, by adjusting the C/Zr ratio to control the pore structure of the porous ceramics, we have achieved simultaneous optimization of mechanical, thermal insulation, and microwave absorption properties in ZrC porous ceramics, meeting the application requirements for multifunctional structural materials in ultra-high-temperature thermal protection.

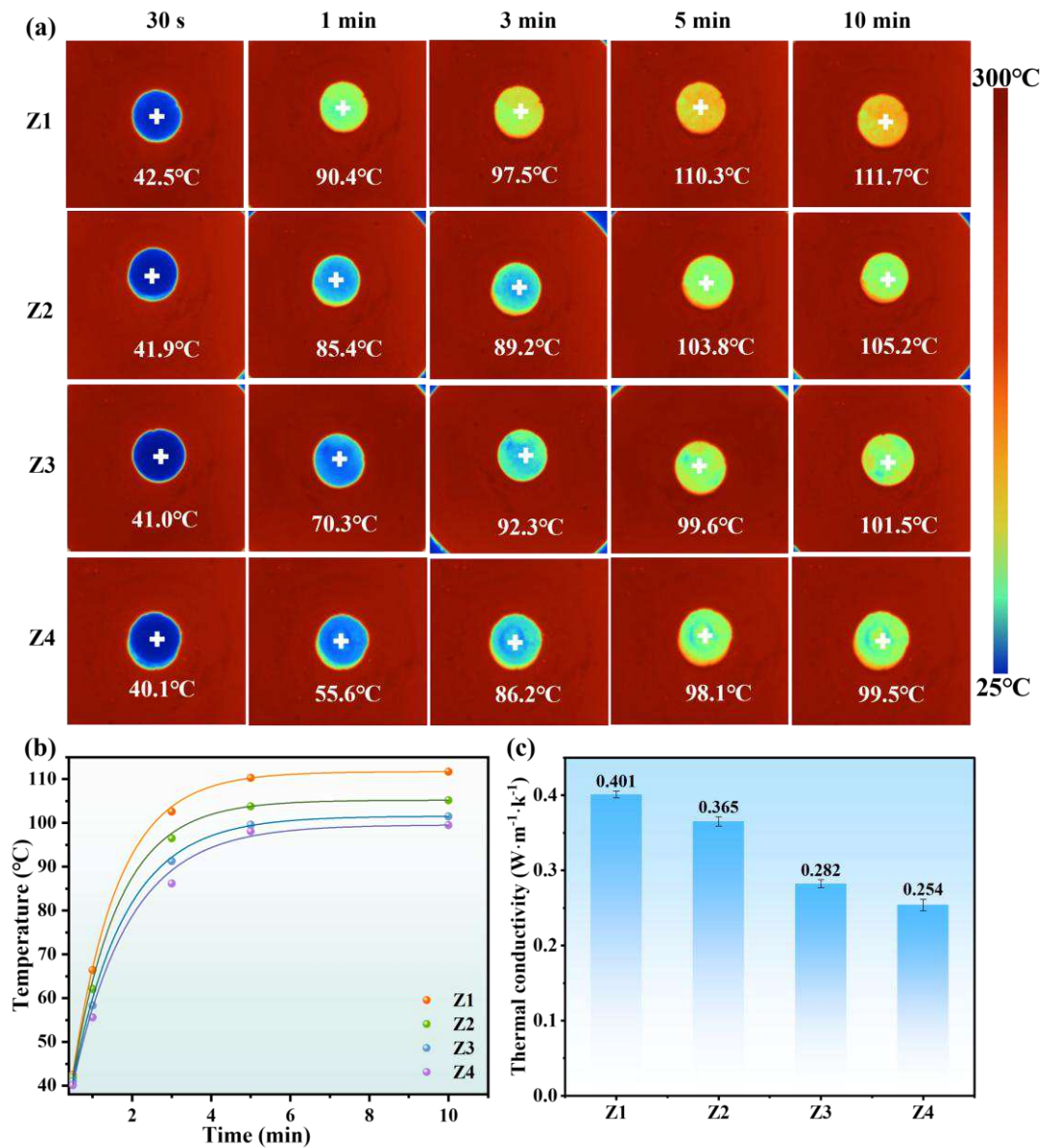


Figure 12 (a) Thermal infrared image of the sample, (b) Cold-side temperature versus time curve, (c) Thermal conductivity.

4 Conclusion

A porous ZrC ceramic with a three-dimensional porous network structure was successfully synthesized using the self-bubbling method, composed of interconnected ZrC microspheres. The influence of the C/Zr ratio on the microstructure and properties of the porous ZrC ceramic was investigated. As the C/Zr ratio increased, the particle size of ZrC microspheres gradually enlarged, and the pore size distribution expanded from 0.6–3 μm to 0.4–6 μm . Porosity increased from 54.6% to 71.0%. By adjusting the

dielectric constant, optimizing impedance matching, and tuning the attenuation constant, samples with different C/Zr ratios collectively enhanced the microwave absorption performance of the porous ZrC ceramic, achieving a minimum reflection loss of -28.87 dB and an effective absorption bandwidth of 5.05 GHz. The microwave absorption mechanism follows the quarter-wavelength interference cancellation principle, resulting from the combined effects of conductive loss, dipolar polarization, and multiple reflections within the porous structure, which endows the material with significant electromagnetic wave absorption capability. Additionally, the compressive strength of the porous ZrC ceramic increased progressively with increasing C/Zr ratio, reaching a maximum of 23.6 MPa. Meanwhile, the high porosity structure confers excellent thermal insulation properties, with a thermal conductivity as low as 0.254 $\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$. This hierarchical pore structure effectively blocks heat transfer pathways, enabling precise optimization of thermal insulation performance. Therefore, increasing the C/Zr ratio simultaneously enhances both mechanical load-bearing capacity and thermal insulation performance while maintaining high porosity and superior microwave absorption properties.

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