

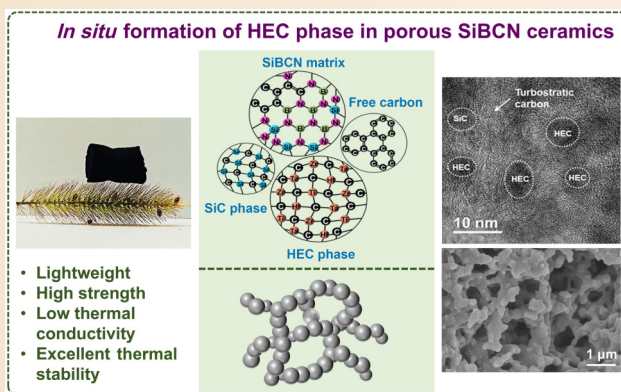
In situ formation of high-entropy carbide phase in porous SiBCN ceramic for enhanced high-temperature stability

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ABSTRACT: Porous SiBCN ceramics exhibit great potential in high-tech structural and functional applications. However, nucleation-crystallization and carbothermal decomposition limit their use in high-temperature environments. Herein, high-entropy carbide (HEC) ($\text{Ti}_{0.25}\text{Zr}_{0.25}\text{Hf}_{0.25}\text{Ta}_{0.25}\text{C}$)-modified porous SiBCN ceramics (HEC/SiBCN) were successfully fabricated from a multi-metal (Ti,Zr,Hf,Ta) precursor containing polyborosilazane via solvothermal methods, freeze-drying, and pyrolysis. The porous HEC/SiBCN ceramic possesses tailorable porosity (63.5%–79.1%), low thermal conductivity (0.054–0.089 W/(m·K)), and good mechanical strength. The HEC phase is *in situ* formed by carbothermal reduction and solid solution reaction of the multicomponent precursor with highly active free carbon in the SiBCN matrix during the pyrolysis, which endows the porous HEC/SiBCN ceramics with outstanding thermal stability up to 1800 °C. The *in situ* formation of the HEC phase provides novel insight and a promising strategy for enhancing the overall performance of porous SiBCN ceramics, expanding their application in high-temperature environments.

KEYWORDS: porous ceramics; high-entropy carbide (HEC) ceramics; SiBCN ceramics; high-temperature stability; thermal insulation



1 Introduction

Porous ceramic materials play indispensable roles as components in important energy- and environment-related fields because of their unique porous structure and strong chemical bonding [1,2], such as thermal insulation/protection, lightweight structures, exhaust filters, molten metal filtration, catalyst supports, energy storage, and electromagnetic shielding. With the advancement of hypersonic vehicles and aerospace industry, it is an urgent and important work at present to develop porous ceramic materials with excellent thermal insulation, thermal stability, and mechanical bearing capacity [3].

Compared with other silicon-based polymer-derived ceramics (PDCs, i.e., SiC, SiOC, and SiCN), SiBCN ceramics display excellent (ultra) high-temperature stability in an inert atmosphere of up to 2000 °C, oxidation resistance in air up to 1600 °C, and creep resistance (0.25% creep strain at 1400 °C), which arises from highly covalent bonding and rigid networks [4,5], and have attracted considerable research interest for thermal-structural applications [6]. To date, a variety of synthesis methods for porous SiBCN ceramics have been explored, such as sacrificial template

[7], direct pyrolysis of polyborosilazane (PBSZ) precursor [8], and porous substrate-guided chemical vapor deposition [9]. The obtained porous SiBCN ceramics exhibit low densities of 0.6–1.5 g/cm³, high porosities of 44%–69%, and high specific surface areas of 31–171 m²/g, which can be employed in environmental and energy applications [7–11]. Specifically, the SiBCN aerogel, as a novel kind of porous material, has been obtained via solvothermal assembly and freeze/supercritical drying, followed by pyrolysis [12]. Compared with traditional porous materials, the SiBCN aerogel possesses unique characteristics, such as low density (0.04–0.22 g/cm³), high porosity (usually ≥ 90%), high specific surface area (66–850 m²/g), and low thermal conductivity (0.025–0.082 W/(m·K)), making it an excellent candidate for high-tech applications, including energy storage, thermal insulation, sensors, and wastewater treatment [13–17]. However, it still falls below the strict requirements for applications in harsh environments because of high-temperature-induced issues such as phase separation, crystallization, and thermal degradation, which cause structural collapse and performance deterioration of porous SiBCN ceramics [16]. Hence, developing porous SiBCN ceramics with excellent thermal and

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structural stability remains a huge challenge for thermal insulation and other functional applications in (ultra)high-temperature environments.

Incorporating transition metals (such as Zr, Ti, Hf, and Al) into SiBCN ceramics has proven to be an effective route to improve high-temperature stability because of the formation of more thermally stable components, such as oxides, carbonitrides, and silicides, in the system [18–20]. For example, Yuan *et al.* [18] obtained HfC/HfB₂/SiC (in argon) and HfN/Si₃N₄/SiBCN (in nitrogen) nanocomposites through pyrolysis of a single-source hafnium-containing PBSZ precursor, providing a novel path toward nanostructured ultrahigh-temperature materials with adjustable composites. Feng *et al.* [19] observed the formation of a stable ZrN phase in the Zr-modified SiBCN ceramics, which resulted in improved thermal stability (mass loss of only 1.7 wt% at 1500 °C) compared with that of pure SiBCN ceramics. However, little attention has been paid to metal element-modified SiBCN ceramics with porous structures. Recently, our team successfully introduced Ti and Zr elements into SiBCN aerogels, which caused the formation of TiCN and ZrC phases in the SiBCN matrix, endowing significant resistance to thermal decomposition and crystallization at temperatures up to 1800 °C [15,21].

Very recently, the combination of high-entropy carbide (HEC) ceramics and PDCs has attracted considerable attention [22,23]. HEC ceramics show high hardness, elastic modulus, oxidation resistance, and low thermal conductivity; thus, these materials are promising for applications in ultrahigh-temperature fields, such as structural materials and thermal insulation/protection [24]. Lu *et al.* [22] prepared a dense monolithic SiC/(Ti_{0.25}Zr_{0.25}Hf_{0.25}Ta_{0.25})C nanocomposite using a multi-metal-containing single-source precursor, which exhibited excellent oxidation resistance with the parabolic oxidation rate constant (K_p) values of 10^{-2} – 10^{-3} mg²/(cm⁴·h) in the range of 1200–1500 °C. Awin *et al.* [23] constructed an HEC phase in amorphous Si-based ceramics using polysiloxane and polycarbosilane as precursors, revealing the effect of the polymer precursor architecture on the structures of the HEC phase at various length scales. This wet chemical route involving co-hydrolysis and polycondensation of metal alkoxides or acetylacetonates provides a novel strategy for introducing HEC phase into SiBCN ceramics for the development of novel SiBCN-based ceramics with outstanding overall performance.

Herein, we successfully prepare (Ti_{0.25}Zr_{0.25}Hf_{0.25}Ta_{0.25})C-modified SiBCN ceramics (labeled HEC/SiBCN) with a porous structure using a multi-metal-containing PBSZ precursor through stepwise hydrothermal reaction, freeze-drying, and pyrolysis. Moreover, the microstructure of the porous HEC/SiBCN ceramics was tuned by adjusting the HEC content and pyrolysis temperature. The structural evolution, mechanical/thermophysical properties, and thermal stability were systematically studied. The HEC phase is formed by carbothermal reduction and solid solution reaction utilizing highly active free-carbon phase in the SiBCN matrix, and the formation temperature is 1600 °C, lower than that of previous HEC-based ceramics produced via the power sintering method (over 2000 °C) [25,26]. The *in situ* formation of the HEC phase endows the porous HEC/SiBCN ceramics with excellent structural stability up to 1800 °C in an Ar atmosphere, broadening its application in high-temperature environments.

2 Experimental

2.1 Raw materials

Zirconium acetylacetonate (Zr(C₅H₇O₂)₄, 98% purity, Shanghai Meryer Biochemical Technology Co., Ltd., China), hafnium

acetylacetonate (Hf(C₅H₇O₂)₄, 97% purity, Shanghai Meryer Biochemical Technology Co., Ltd., China), tetrabutyl titanate (Ti(C₄H₉O)₄, 99.7% purity, Shanghai Aladdin Biochemical Technology Co., Ltd., China), and tantalum ethoxide (Ta(C₂H₅O)₅, 99.9% purity, Tianjin Hiens Optus Technology Co., Ltd., China) were utilized as multi-metal sources for the HEC precursor. Polyborosilazane (PBSZ, Institute of Chemistry, Chinese Academy of Sciences, China) was utilized as the precursor, and divinylbenzene (DVB, 80% isomer mixture, Beijing Bailingwei Technology Co., Ltd., China) was used as a crosslinking agent to fabricate carbon-rich SiBCN ceramics. The structural formula of the PBSZ precursor is shown in Fig. S1 in the Electronic Supplementary Material (ESM), and the chemical composition (atomic ratio) of the obtained carbon-rich SiBCN ceramics is as follows: Si (6.3%), B (not detected (nd)), C (87.6%), N (5.1%), and O (1%) pyrolyzed at 1400 °C, as determined by energy dispersive spectroscopy (EDS). Cyclohexane (C₆H₁₂, 99.7% purity) and *n*-butyl alcohol (CH₃(CH₂)₃OH, 99.7% purity) as the solvents were purchased from Tianjin Kemiou Chemical Co., Ltd., China.

2.2 Preparation of porous HEC/SiBCN ceramics

Porous HEC/SiBCN ceramics were prepared by the solvothermal method, followed by freeze-drying and pyrolysis. First, 1.22 g of Zr(C₅H₇O₂)₄, 1.44 g of Hf(C₅H₇O₂)₄, 0.85 g of Ti(C₄H₉O)₄, and 1.02 g of Ta(C₂H₅O)₅ were dissolved in 25.6 g of *n*-butyl alcohol by stirring for 1 h in an oil bath at 140 °C under an argon atmosphere. The mole ratios of the four metals (Ti, Zr, Hf, and Ta) are equal. The *n*-butyl alcohol mixture was then evaporated at 80 °C for 1 h to obtain a yellow viscous liquid called HEC precursor. Second, 1 g of PBSZ precursor, 1 g of DVB, and 1 g of HEC precursor were dissolved in 17 g of cyclohexane by magnetic stirring for 1 h in a flow of argon at room temperature. Then, the mixed solution was further transformed into a Teflon-lined autoclave for solvothermal reaction at 150 °C for 20 h to obtain a HEC/PBSZ wet gel. Next, the wet gel was soaked in cyclohexane to remove residues for 3–5 d until the solution was clear. Afterward, the HEC/PBSZ wet gel was frozen at –50 °C for 30 min and then freeze-dried for 48 h to form a porous HEC/PBSZ precursor. Finally, the porous HEC/SiBCN ceramics were obtained by pyrolysis at different temperatures (1200, 1400, 1600, and 1800 °C) for 2 h under argon atmosphere with a heating rate of 5 °C/min.

The porous HEC/SiBCN ceramics were prepared from different mass ratios of HEC to PBSZ of 0.5, 1, and 2 and denoted as HEC/SiBCN-*X*, where *X* is the mass ratio of HEC:PBSZ. The pure SiBCN ceramics were prepared without the addition of HEC precursor for comparison.

2.3 Characterizations

The porosity (*P*) values of the HEC/PBSZ precursor and porous HEC/SiBCN ceramics were calculated via Eq. (1):

$$P = (1 - \rho/\rho_t) \times 100\% \quad (1)$$

where ρ is the apparent density and ρ_t is the theoretical density. For the HEC/PBSZ precursor, the apparent density was obtained by measuring the dimension and mass of three samples, and the theoretical density is 1.2 g/cm³. For the porous HEC/SiBCN ceramics, the apparent density was measured by Archimede's method, and the theoretical density was calculated by the volume ratio of the HEC phase to the SiBCN phase based on XPS results and the theoretical densities of the HEC and SiBCN ceramics (10.05 g/cm³ [27] and 2.0 g/cm³ [28], respectively). The density was tested on three parallel samples to obtain an average value.

The chemical structures of the porous HEC/SiBCN ceramics were characterized by a Fourier transform infrared spectrometer (FT-IR; Thermo Fisher Nicolet iS5, USA) and an X-ray photoelectron spectroscope (XPS; Axis Supra, UK). The micromorphology was determined by a field-emission scanning electron microscope (FE-SEM; S4800, Hitachi, Japan) and a field-emission transmission electron microscopy (TEM; JEOL-200CX, JEOL, Japan) equipped with energy dispersive spectroscopy (EDS). The phase composition was characterized by an X-ray diffractometer (XRD; D8 Advance, Bruker, Germany) with Cu K α radiation ($\lambda = 1.54 \text{ \AA}$) over a 2θ range of 10° – 90° at a scanning speed of $0.12^\circ/\text{s}$, and the Debye–Scherrer equation [29] was used to calculate the grain sizes of the HEC and SiC phases, as shown in Eq. (2):

$$D = (K\lambda) / (\beta \cos\theta) \quad (2)$$

where λ is the X-ray wavelength (nm); β is the peak width of the diffraction peak profile at the half maximum height resulting from the small crystallite size in radians; K is a constant related to the crystallite shape, normally taken as 0.9.

The thermal conductivity of the HEC/SiBCN samples was measured by the hot-wire method (TC3000, Xiotech, China) at room temperature using the powder of HEC/SiBCN samples. The compressive strength was tested by a universal testing machine (LD24.204, Lishi, China) on the samples with dimensions of approximately $\phi 8 \text{ mm} \times 4 \text{ mm}$ under a loading speed of 0.2 mm/min . The test was performed on two parallel samples to obtain an average value. To evaluate the high-temperature stability, the porous HEC/SiBCN ceramics were treated at 1600 and 1800°C in argon for 2 h at a heating rate of 5°C/min , and their structural evolution and physical, mechanical, and thermal properties were studied. The oxidation behavior was analyzed via a thermogravimetric analyzer (TGA; Netzsch STA 449F3, Germany) from room temperature to 1400°C at a heating ramp of 10°C/min in flow air with a flow rate of 254 mL/min .

3 Results and discussion

3.1 Synthesis and structure of HEC/PBSZ precursor

The preparation process of porous HEC/SiBCN ceramics can be divided into three steps: wet-chemical synthesis of HEC precursor, assembly of porous HEC/PBSZ precursor, and organic-to-inorganic transformation to porous HEC/SiBCN ceramics, as shown in Fig. 1. The HEC precursor was synthesized via alcoholysis and polycondensation reactions from transition-metal alkoxides and acetylacetonates, as shown in Fig. 1(a), which was verified with the M–O–M bond at 645 cm^{-1} [30] in the FTIR spectra (Fig. S2 in the ESM). During the solvothermal process, the PBSZ precursor formed a three-dimensional porous network through hydrosilylation and dehydrogenation coupling reactions using DVB as a crosslinker. Moreover, the HEC precursor was incorporated into the PBSZ network through reactions between the M–OR groups and active groups in the network (e.g., Si–H) [18,31]. During the freeze-drying process, the cyclohexane solvent in the obtained HEC/PBSZ wet gel was sublimated to yield a porous HEC/PBSZ precursor. Finally, the porous HEC/PBSZ precursor underwent organic-to-inorganic transformation during the follow-up pyrolysis to form porous HEC/SiBCN ceramics, accompanied by the formation of a HEC phase in the SiBCN matrix through carbothermal reduction and a solid solution reaction, as illustrated in Fig. 1(b). The HEC/SiBCN ceramics possess a porous structure with aggregated nanoparticles formed during the solvothermal and freeze-drying processes, which are affected by several preparation parameters, such as reactant concentration, DVB content, and solvothermal and freezing temperatures [15,17,21]. In addition, the pyrolysis temperature and the HEC content also affect the porous structure of the HEC/SiBCN ceramics, which will be discussed in Section 3.2.

The densities of the porous HEC/PBSZ precursors are in the range of 0.066 – 0.090 g/cm^3 and decrease with increasing HEC content, as shown in Fig. 2(a), and the porosities are in the range

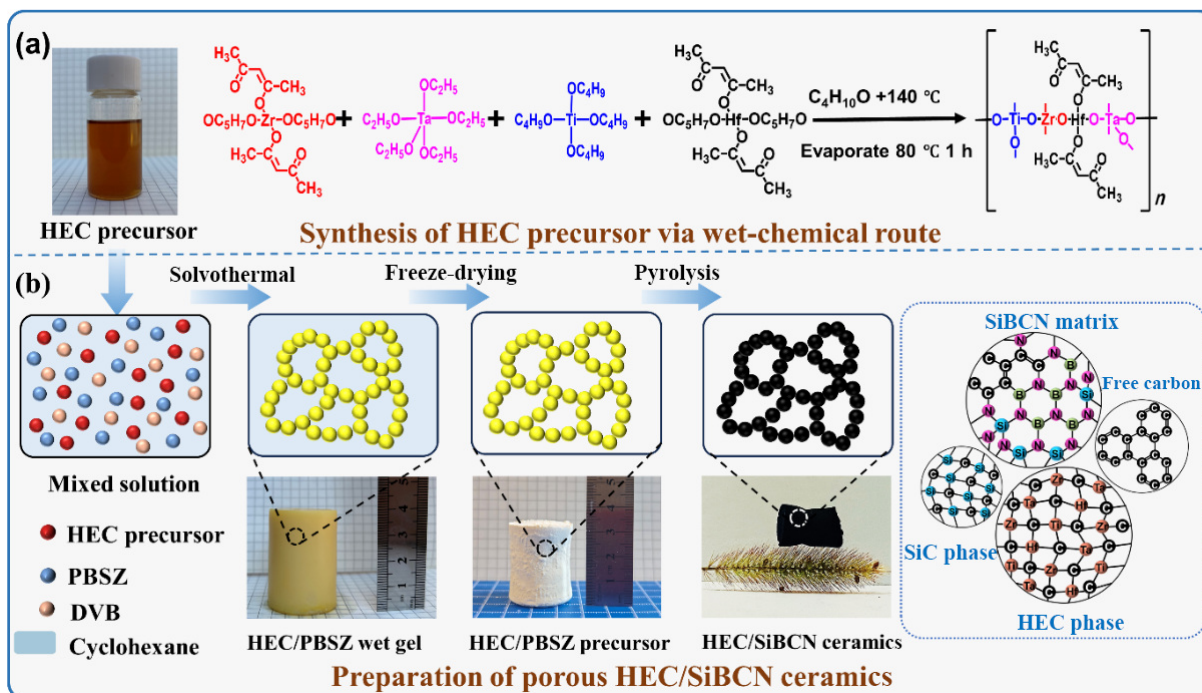


Fig. 1 Schematic diagram of process used to fabricate porous HEC/SiBCN ceramics: (a) wet-chemical synthesis of HEC precursor and (b) porous HEC/SiBCN ceramics obtained via solvothermal and freeze-drying and organic-to-inorganic conversion through pyrolysis.

of 92.5%–94.5%, indicating the super-porous characteristics of the precursor. The chemical structures of the HEC/PBSZ precursors with different HEC contents were characterized with FT-IR spectroscopy, as shown in Fig. 2(b). The HEC/PBSZ precursors retain the backbone of the PBSZ precursor, which consists of Si–N–B bonds (842 cm^{-1}), B–N bonds (1467 cm^{-1}), Si–N–Si bonds (889 cm^{-1}), and Si–C bonds (751 cm^{-1}) [19]. Additionally, the intensities of the Si–H and N–H bonds decrease with increasing HEC content, demonstrating the reactions between the HEC precursor and the PBSZ precursor, such as $\text{Si-H} + \text{M-OR} \rightarrow \text{Si-O-M} + \text{RH}$ and $\text{N-H} + \text{M-OR} \rightarrow \text{N-M} + \text{ROH}$ [23].

The chemical bonding of the HEC/PBSZ precursor was further analyzed by XPS, as shown in Figs. 2(c)–2(i). Si–N at 102.1 eV and Si–C at 101.1 eV are observed in the Si 2p XPS spectrum (Fig. 2(c)), and B–N at 398.8 eV is observed in the N 1s XPS spectrum (Fig. 2(d)), confirming the existence of the backbone of the PBSZ precursor. Furthermore, the Si–O peak (Si 2p: 103.3 eV) is slightly lower than the reported peak (Si–O: 103.5 eV) in the Si 2p spectra, corresponding to the formation of Si–O–M bonds. Generally, metallic elements have lower electronegativity than Si, leading to a shorter bond length of Si–O–M [32], causing a shift in the binding energy. The Si–O–M bond at 532.4 eV was also observed in the O 1s spectra (Fig. 2(e)), further confirming the chemical reactions between PBSZ and the HEC precursor [23]. The four metallic elements (Figs. 2(f)–2(i)) in the HEC/PBSZ

precursor exist in the form of metal–oxygen bonds (M–O), corresponding to the Ta–O peak (Ta $4f_{5/2} = 26.07\text{ eV}$, Ta $4f_{7/2} = 27.97\text{ eV}$), Ti–O peak (Ti $2p_{1/2} = 458.7\text{ eV}$, Ti $2p_{3/2} = 464.7\text{ eV}$), Zr–O peak (Zr $3d_{3/2} = 182.42\text{ eV}$ and Zr $3d_{5/2} = 184.82\text{ eV}$), and Hf–O peak (Hf $4f_{5/2} = 14.51\text{ eV}$ and Hf $4f_{7/2} = 16.01\text{ eV}$) [33–35], which are highly consistent with the structure of the HEC precursor. In addition, C–C bond (284.8 eV) as the main structure was observed in the C 1s spectra of the precursor (Fig. S3 in the ESM), as well as small amounts of C–O bond (286.1 eV) and C–Si bond (283.9 eV), which mainly come from the side chain ligands of PBSZ and HEC precursors.

3.2 Structural evolution of porous HEC/SiBCN ceramics

The HEC/PBSZ precursors were further pyrolyzed at different temperatures ($1200\text{--}1800\text{ }^{\circ}\text{C}$) in a flow of argon to form porous HEC/SiBCN ceramics, and their densities, porosities, ceramic yields, and linear shrinkages are shown in Fig. 3. The density of HEC/SiBCN-1 increases from 0.55 to 0.91 g/cm^3 with increasing pyrolysis temperature, accompanied by a similar porosity from 73.1% to 76.8% (Fig. 3(a)). The ceramic yield slightly decreases from 27.25% to 21.63% with increasing linear shrinkage (from 59.81% to 70.26%) at elevated temperatures, as shown in Fig. 3(b). Furthermore, porous HEC/SiBCN ceramics with different HEC contents were obtained by pyrolysis at $1400\text{ }^{\circ}\text{C}$, and their densities are in range of $0.74\text{--}0.79\text{ g/cm}^3$, with little effect on the HEC

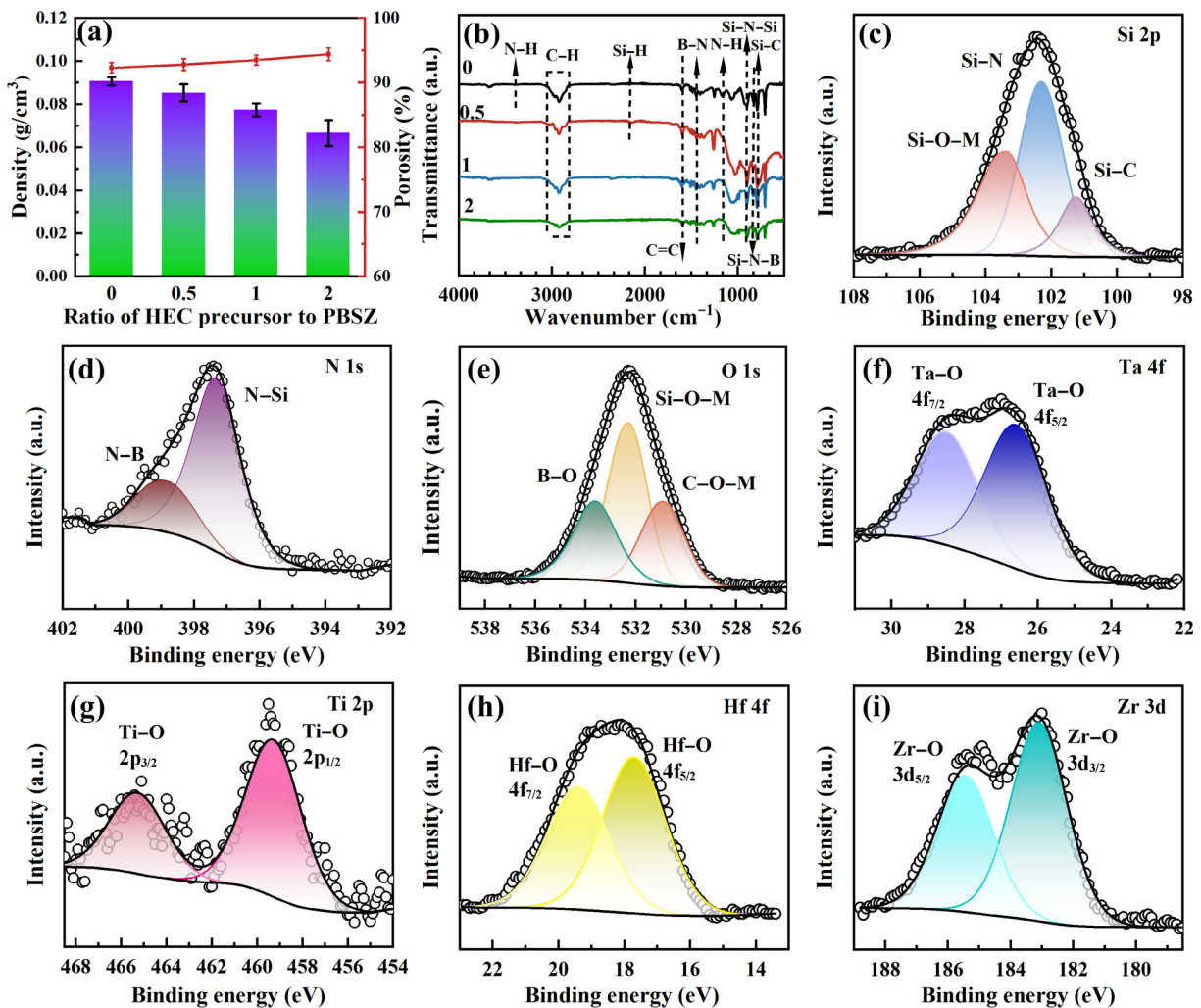


Fig. 2 (a) Density and porosity; (b) FT-IR spectra of HEC/PBSZ precursors with different contents of HEC precursor; XPS spectra of HEC/PBSZ-1: (c) Si 2p, (d) N 1s, (e) O 1s, (f) Ta 4f, (g) Ti 2p, (h) Hf 4f, and (i) Zr 3d.

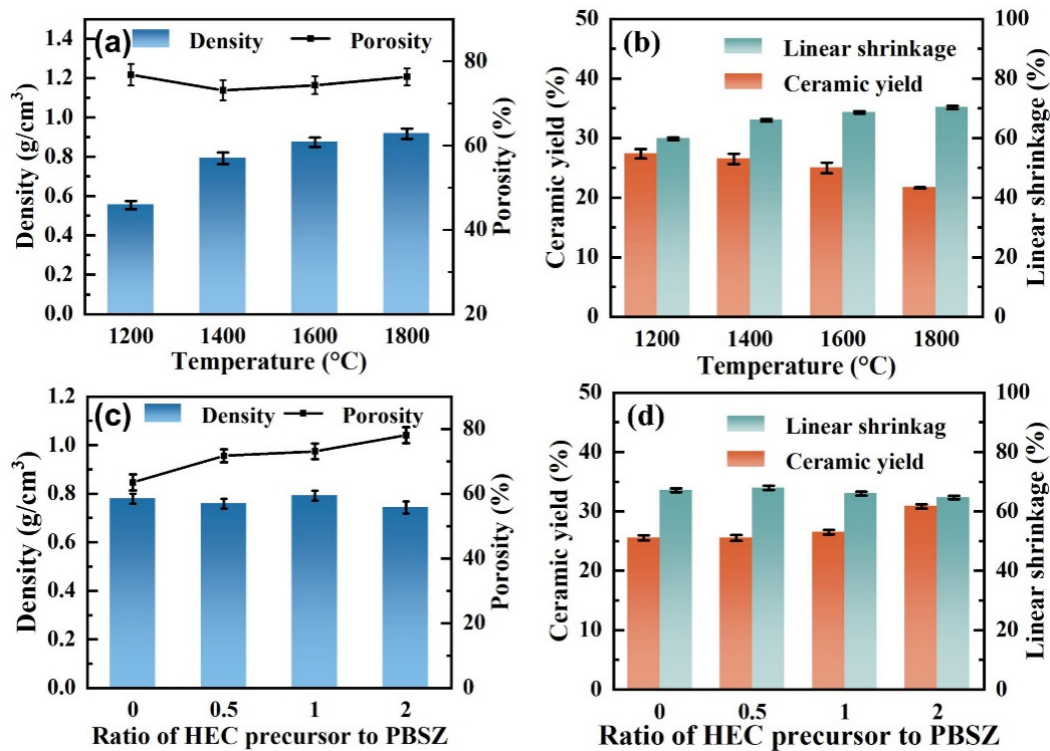


Fig. 3 (a, c) Density and porosity and (b, d) ceramic yield and linear shrinkage of the HEC/SiBCN ceramics: (a, b) HEC/SiBCN-1 pyrolyzed at different temperatures and (c, d) HEC/SiBCN ceramics with different HEC contents pyrolyzed at 1400 °C.

content, as shown in Fig. 3(c). In contrast, the porosities of the HEC/SiBCN ceramics are greater than those of the pure SiBCN ceramics and increase from 63.5% to 79.1% with increasing HEC ratio, which can be attributed to the much greater density of the HEC phase than the SiBCN phase. Moreover, there is a slight increase in the ceramic yield (25%–31%) and a small change in the linear shrinkage (64%–68%) with increasing HEC content, as shown in Fig. 3(d), indicating little effect of the introduced HEC precursor on the ceramic transformation process of the porous SiBCN ceramics.

Figure 4 presents SEM images of porous HEC/SiBCN ceramics at different pyrolysis temperatures and with different HEC contents. All the samples present a typical pearl necklace-like (or aerogel-like) structure with aggregated nanoparticles and high porosity. With increasing pyrolysis temperature, HEC/SiBCN-1 maintains an aerogel-like structure, indicating structural stability during the pyrolysis (Figs. 4(a)–4(f)). However, the skeleton of the porous structure seems coarsen at an elevated temperature of 1800 °C (Figs. 4(c) and 4(f)), suggesting slight sintering of the nanoparticles. Moreover, the porous skeleton in the HEC/SiBCN ceramics gradually coarsens with increasing HEC content, indicating that the thickness of the skeleton in HEC/SiBCN-2 (~450 nm, Fig. 4(i)) triples that of HEC-0.5 (~150 nm, Fig. 4(h)). The HEC precursor may decrease the nucleation rate of the PBSZ nanoparticles during the solvothermal process due to the steric hindrance effect and tend to form a coarse network in the system [13]. Elemental mapping reveals that all the elements are distributed homogeneously in the porous HEC/SiBCN ceramics (Fig. S4 in the ESM). Clearly, the atomic ratios of Ti, Zr, Hf, and Ta metal elements are approximately equal (Table S1 in the ESM), and their contents increase with the addition of the HEC precursor to the system.

To investigate the phase evolution during the pyrolysis, the porous HEC/SiBCN ceramics pyrolyzed at different temperatures

were characterized by XRD (Fig. 5). For the pure SiBCN ceramic pyrolyzed at 1200–1400 °C, a broad peak at $2\theta = 23.2^\circ$ corresponds to the amorphous SiBCN phase (Fig. S5 in the ESM). In addition, the band in the range of 22° – 25° is typically observed in different carbon materials attributed to the (002) plane of carbon phase [36], suggesting the existence of free carbon in the system. When the pyrolysis temperature is increased to 1600 °C, weak diffraction peaks appear at 35.74° , 60.19° , and 71.98° , corresponding to (111), (220), and (311) of β -SiC (3C, PDF#39-1196), respectively. The crystalline size and crystallinity of β -SiC phase further increase at 1800 °C, accompanied by the formation of the B(C)N phase (PDF#85-1068) at 26.2° . Such analysis suggests that carbothermal reduction can occur between oxygen- or nitrogen-containing phases (e.g., $\text{SiO}_x\text{C}_{4-x}$ and $\text{SiC}_x\text{N}_{4-x}$) and free carbon at elevated temperatures ($> 1450^\circ\text{C}$), leading to the formation and grain growth of SiC nanocrystals in the amorphous SiBCN matrix [37].

In clear contrast, porous HEC/SiBCN ceramics undergo sequential formation of various metal oxides followed by the formation of metal carbides and multi-component solid solutions of metal carbides at elevated temperatures during pyrolysis (Fig. 5). For example, HEC/SiBCN-0.5 pyrolyzed at 1200 °C shows the presence of m-ZrO₂ (PDF#37-1484) and HfO₂ (PDF#78-0050) at 28.34° , 31.65° , and 50° , and the peak at 30° corresponds to solid oxide solutions (including (Ti,Zr)O_x, (Ti,Hf)O_x, and (Hf,Ta)O_x) [30,38] (Fig. 5(a)). At 1400 °C, the oxides were transformed into solid solutions of multi-metal carbides with characteristic peaks at 34.6° , 40.5° , and 58.8° [30,38], demonstrating the occurrence of carbothermal reduction reactions between metal oxides and free carbon in the SiBCN matrix. In addition, the (Ti,Ta)C phase was also observed at 1200 °C due to the low formation temperature of TiC and TaC phases through the carbothermal reaction, which will be discussed later. As the temperature is increased to 1600 °C, the diffraction peaks

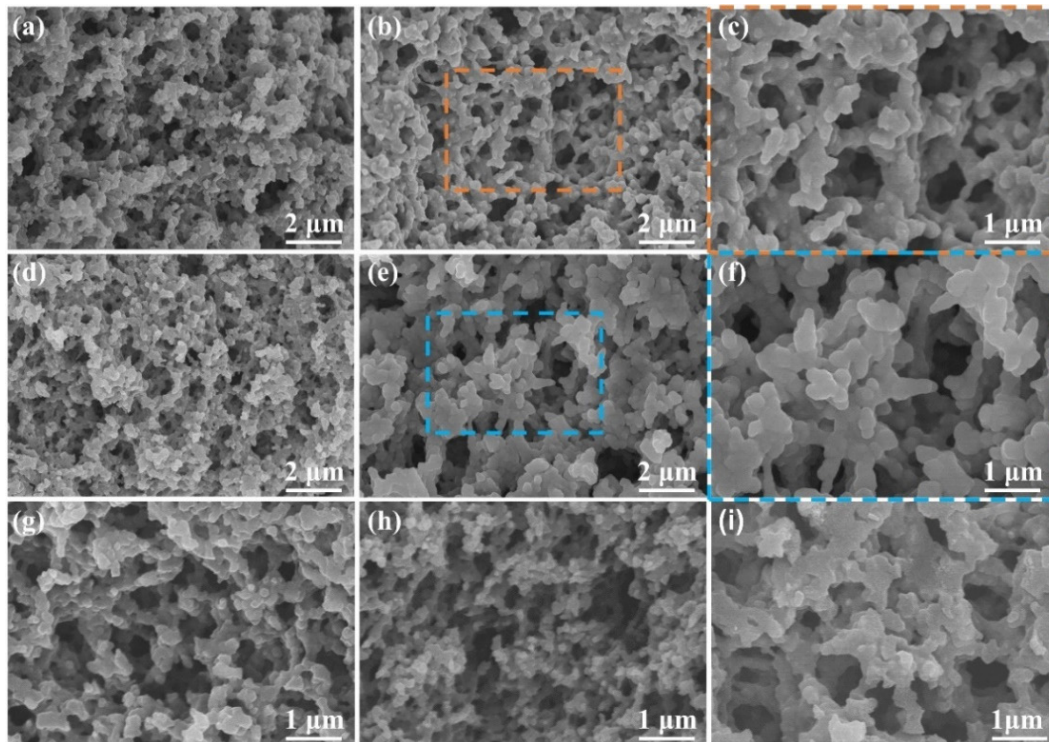


Fig. 4 SEM images of HEC/SiBCN-1 pyrolyzed at different temperatures: (a) 1200 °C, (b, c) 1400 °C, (d) 1600 °C, and (e, f) 1800 °C; SEM images of HEC/SiBCN ceramics with different HEC contents pyrolyzed at 1400 °C: (g) pure SiBCN; (h) HEC/SiBCN-0.5, and (i) HEC/SiBCN-2.

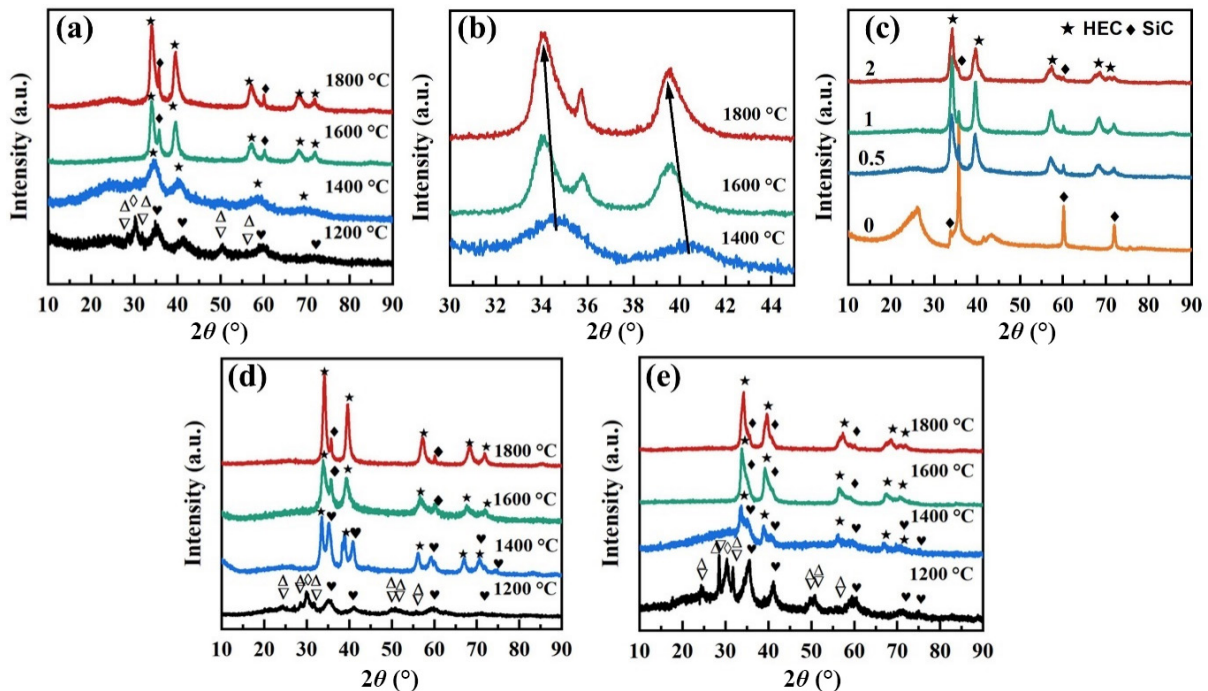


Fig. 5 XRD patterns of HEC/SiBCN ceramics: (a) HEC/SiBCN-0.5 pyrolyzed at different temperatures, (b) partial enlargement of (a), (c) HEC/SiBCN ceramics with different HEC contents pyrolyzed at 1800 °C, and (d) HEC/SiBCN-1 and (e) HEC/SiBCN-2 pyrolyzed at different temperatures. Symbols in (a–e): ★, carbide solid solutions; ◆, β -SiC; ♥, (Ti,Ta)C; ▽, m-ZrO₂; △, HfO₂; ◇, (Ti,Zr)O_x, (Ti,Hf)O_x, (Hf,Ta)O_x.

of the HEC were clearly observed at 33.9°, 39.6°, and 57.1°, of which the intensities increase at 1800 °C, showing a characteristic face-centered cubic crystal structure [38] (FCC, Fig. S6 in the ESM). Notably, the diffraction peaks of the HEC phase shift to lower 2θ values with increasing temperature, corresponding to the increased interplanar spacing of the HEC phase, as shown in Fig. 5(b), which is consistent with the results of a previously

reported work [38]. The subsequent XPS results confirm that the number of M–O bonds decreases with increasing pyrolysis temperature in the HEC/SiBCN ceramics. Therefore, it is reasonable to assume that dissolved oxygen atoms exist in the HEC lattice, which are gradually replaced by carbon atoms at high pyrolysis temperatures, accompanied by the continuous occurrence of carbothermal reduction reaction.

Moreover, the β -SiC phase was also detected in the HEC/SiBCN ceramics with different HEC contents as the pure SiBCN ceramics, but the intensity of the SiC phase is smaller, as shown in Fig. 5(c). The grain sizes of the SiC crystals in the HEC/SiBCN ceramics are in the range of 9.5–12.7 nm according to the Scherrer equation [29], which is much smaller than that of pure SiBCN ceramics (22.6 nm), indicating that the introduction of the HEC phase affects the growth of the SiC crystals in the ceramics. The formation of HEC consumes a part of free carbon, affecting the carbothermal reduction reaction of oxygen- and nitrogen-containing phases with free carbon [37]. In addition, the high-entropy multi-component system reduces the atomic migration rate, which also plays a role in stabilizing the amorphous structure of the SiBCN matrix.

HEC/SiBCN-1 and HEC/SiBCN-2 (Figs. 5(d) and 5(e)) exhibit a similar phase evolution during the pyrolysis (1200–1800 °C) from various metal oxide phases to oxidize solid solutions to the HEC phase. In contrast, the complete transformation of (Ti,Ta)C phase to HEC phase occurs at a higher temperature (1600 °C) than that of HEC/SiBCN-0.5 (1400 °C), which should be related to the increased TiC and TaC phases in the system. Moreover, there are some differences between HEC/SiBCN-1 and HEC/SiBCN-2 under careful observation. For 1200 °C-pyrolyzed samples, the intensities of the diffraction peaks of metal oxides in HEC/SiBCN-2 are higher than those in HEC/SiBCN-1, indicating the formation of more metal oxides. Additionally, the peaks of SiC and HEC partially overlap in 1800 °C-pyrolyzed HEC/SiBCN-2, which may be caused by the entrance of Si atoms into the HEC lattice [23]. Notably, the formation of the HEC phase in the SiBCN ceramics occurs at a lower temperature (1600 °C) than previously reported works up to 2000 °C [25,26]. The highly porous structure of the HEC/SiBCN ceramics could increase the activity and migration of the atoms on the wall of the pores to accelerate the carbothermal reduction of metal oxides, thus reducing their onset temperature to a lower temperature [37,39]. Moreover, the chelated metal cations are uniformly distributed in the HEC/PBSZ precursor at the molecular level via the solvothermal route so that adjacent atoms could directly crystallize to form the HEC phase through short-range diffusion.

To study the surface chemistry of the HEC/SiBCN ceramics, XPS surveys were performed on HEC/SiBCN-1 samples pyrolyzed at different temperatures (Fig. S7 in the ESM). The Si 2p spectra (Fig. 6(a)) suggests that the porous HEC/SiBCN ceramics mainly consist of Si–N bond at 101.7 eV together with a small amount of Si–C bond at 100.8 eV and Si–O bond at 103.3 eV [32]. The main peak shifts from 102.1 to 101.5 eV with increasing pyrolysis temperature, indicating the transformation from Si–N bond to Si–C bond during pyrolysis. Moreover, the Si–C component increases with increasing pyrolysis temperature, accompanied by a decrease in the Si–N and Si–O components, further indicating the formation of the SiC phase during pyrolysis, which is consistent with the XRD analysis. The C 1s spectrum shows that the C–C bond at 284.8 eV is the main structure for the free-carbon phase in the HEC/SiBCN ceramics and that a small number of C–O–C bonds are present at 285.8 eV (Fig. 6(b)). The C–M/Si bond is also observed at 283.7 eV, corresponding to metal carbide phases, which become more intense as the temperature is increased from 1200 to 1800 °C. Moreover, the C–M peak (Ta–C, Ti–C, Hf–C, and Zr–C) gradually increases with increasing temperature, accompanied by a decrease in the M–O peak (Ta–O, Ti–O, Hf–O, and Zr–O) in the spectra of Ta 4f, Ti 2p, Hf 4f, and Zr 3d (Figs. 6(c)–6(f)), further indicating that the M–O bonds are transformed into M–C bonds via carbothermal reduction.

Therefore, the carbothermal reduction reaction and the solid solution reaction gradually occur in the porous HEC/SiBCN ceramics during pyrolysis.

Moreover, Ta–C and Ta–O bonds appear at 23.09 eV (Ta 4f_{5/2}) and 25 eV (Ta 4f_{7/2}), 26.07 eV (Ta 4f_{5/2}) and 27.97 eV (Ta 4f_{7/2}) in the Ta 4f spectra, respectively (Fig. 6(c)), and Ti–C and Ti–O bonds at 454.7 eV (Ti 2p_{1/2}) and 460.8 eV (Ti 2p_{3/2}), 458.7 eV (Ti 2p_{1/2}) and 464.7 eV (Ti 2p_{3/2}) in Ti 2p, respectively (Fig. 6(d)) [33–35]. With elevated temperature from 1200 to 1800 °C, the intensities of Ti–C and Ta–C peaks gradually increase, whereas the intensities of the Ti–O and Ta–O peaks decrease. In the high-resolution spectra of Zr 3d and Hf 4f (Figs. 6(e) and 6(f)), Zr and Hf only exist in the form of Zr–O (Zr 3d_{3/2} = 182.42 eV and Zr 3d_{5/2} = 184.82 eV) and Hf–O (Hf 4f_{5/2} = 17.03 eV and Hf 4f_{7/2} = 18.72 eV) bonds at 1200 °C, and Zr–C (Zr 3d_{3/2} = 179.07 eV and Zr 3d_{5/2} = 182.50 eV) and Hf–C bonds (Hf 4f_{5/2} = 14.51 eV and Hf 4f_{7/2} = 16.01 eV) [33–35] are detected when pyrolyzed at 1400 °C, and the intensity of the carbides gradually increases as the temperature increases to 1800 °C. These results confirm the preliminary formation of TiC and TaC phases (1200 °C) in comparison with the ZrC and HfC phases (1400 °C) during pyrolysis, which is consistent with the XRD results.

Figure 7 shows the TEM images and selected-area electron diffraction (SAED) pattern of HEC/SiBCN-1 pyrolyzed from 1400 to 1800 °C. The HEC/SiBCN-1 consists of an amorphous SiBCN matrix decorated with few nanocrystals (Figs. 7(a)–7(c)), which increases with the HEC ratio in the precursor (Fig. S8 in the ESM). Elemental mapping (Fig. S9 in the ESM) shows the existence of the nanocrystals in the SiBCN matrix, and all the metal elements are homogeneously distributed in these nanocrystals corresponding to the HEC phase. The nanocrystals are polycrystalline and mainly contain the HEC phase and SiC phase (Figs. 7(d)–7(f)). Moreover, the HRTEM images (Figs. 7(g)–7(i)) reveal the presence of HEC nanocrystals, small numbers of SiC nanocrystals, and turbostratic carbon, and the grain size of the HEC nanocrystals slightly increases from ~4 nm at 1400 °C to ~11 nm at 1800 °C. The periodic lattice structure of the HEC phase is clearly observed in the porous HEC/SiBCN ceramics obtained at different temperatures (Figs. 7(g)–7(i)), with lattice fringes of 0.230 nm for crystal planes of (200) and 0.263 nm for crystal planes of (111), which is well consistent with the results from Vegard's law ($a = 0.452$ nm) [38]. Notably, the lattice fringes of HEC(111) increase slightly from 0.263 nm (Fig. 7(h)) to 0.265 nm (Fig. 7(i)) with increasing temperature, which is in good agreement with the XRD analysis. Some SiC nanocrystals are also observed in the amorphous SiBCN matrix, as shown in Figs. 7(h) and 7(i), but both the size and number are smaller than those in the pure SiBCN ceramics, which further implies the inhibition of the formation of the SiC phase in the HEC/SiBCN ceramics.

Combined with the above analysis, the HEC phase in the porous SiBCN ceramics should form through *in situ* carbothermal reduction of the HEC precursor and free carbon of the SiBCN matrix during pyrolysis. Based on thermodynamic calculations (Fig. 8(a)), the formation process of the HEC phase is speculated in detail, as shown in Fig. 8(b). Single- and multi-metal oxides (i.e., m-ZrO₂, HfO₂, (Ti,Zr)O_x, (Ti,Hf)O_x, and (Hf,Ta)O_x) are first formed at a low temperature of 1200 °C by decomposition of the HEC precursor. The formation temperatures of TiC (1107.4 °C) and TaC (1287 °C) are much lower than those of HfC (1647.5 °C) and ZrC (1668.7 °C) according to thermodynamic calculations (Fig. 8(a)), so the (Ti,Ta)C phase is preferentially formed at this stage rather than the HfC and ZrC phases, which is consistent with the XRD and XPS results. Next, the metal oxides are

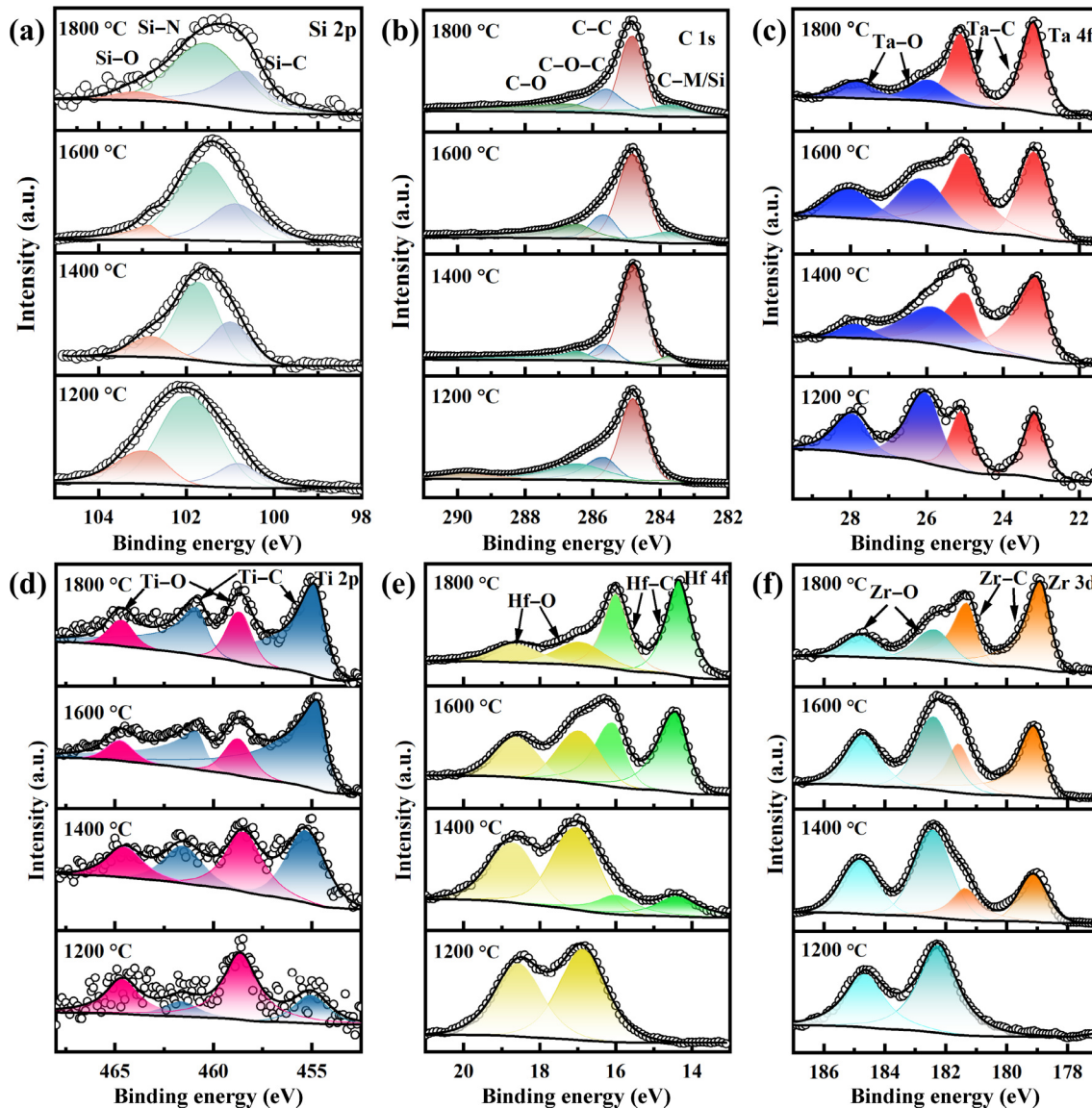


Fig. 6 XPS spectra of HEC/SiBCN-1 pyrolyzed at different temperatures: (a) Si 2p, (b) C 1s, (c) Ta 4f, (d) Ti 2p, (e) Hf 4f, and (f) Zr 3d.

gradually reduced to form carbides and then diffuse to the crystal lattice of carbide solid solutions at 1400 °C, yet some oxygen should still exist in the lattice of the solid solution at this stage. Then, the carbothermal reduction continues at elevated temperatures, and the dissolved oxygen in the lattice is gradually replaced by carbon to form the HEC phase of $(\text{Ti}_{0.25}\text{Zr}_{0.25}\text{Hf}_{0.25}\text{Ta}_{0.25})\text{C}$ in the SiBCN matrix above 1600 °C, which is confirmed by the appearance of the diffraction peaks of carbide solid solutions and absence of oxides in the XRD patterns (Fig. 5).

3.3 Thermal insulation and compressive strength of porous HEC/SiBCN ceramics

Thermal transport in porous materials follows three major modes of heat transfer, including solid conduction, gas conduction, and radiation, in which radiative thermal conductivity can be neglected at room temperature. Therefore, the thermal conductivity of the porous HEC/SiBCN ceramics mainly depends on the phase component and the porosity. The thermal conductivity of HEC/SiBCN-1 obtained at different pyrolysis temperatures ranges from 0.054 to 0.089 W/(m·K), as shown in

Fig. 9(a), and the 1600 °C-pyrolyzed sample has the lowest thermal conductivity of 0.054 W/(m·K) among all the samples. As shown in Fig. 9(b), the porous HEC/SiBCN ceramics with different HEC contents all possess low thermal conductivity (0.049–0.061 W/(m·K)) in comparison with the pure porous SiBCN ceramic (0.09 W/(m·K)), which can be attributed mainly to their higher porosities than the pure SiBCN ceramics (72.2%–79.1% vs. 64.1%, Table S3 in the ESM). Interestingly, the thermal conductivity of the HEC/SiBCN ceramics increases slightly from 0.049 to 0.061 W/(m·K) with increasing HEC content, which is contrary to the change in porosity. The increased HEC content accelerates the formation of the HEC phase in the ceramics, and its higher thermal conductivity than that of the SiBCN matrix may lead to increased solid thermal conductivity in the ceramics.

To evaluate the mechanical properties of the porous HEC/SiBCN ceramics, a uniaxial compression test was conducted. All the HEC/SiBCN ceramics are characterized by the typical fracture behavior of the brittle material, showing that it breaks suddenly under a certain stress (Fig. S10 in the ESM). The compressive strength of the porous HEC/SiBCN ceramics is in the range of (20.5 ± 14.9) – (24.6 ± 7.8) MPa, and the maximal strength

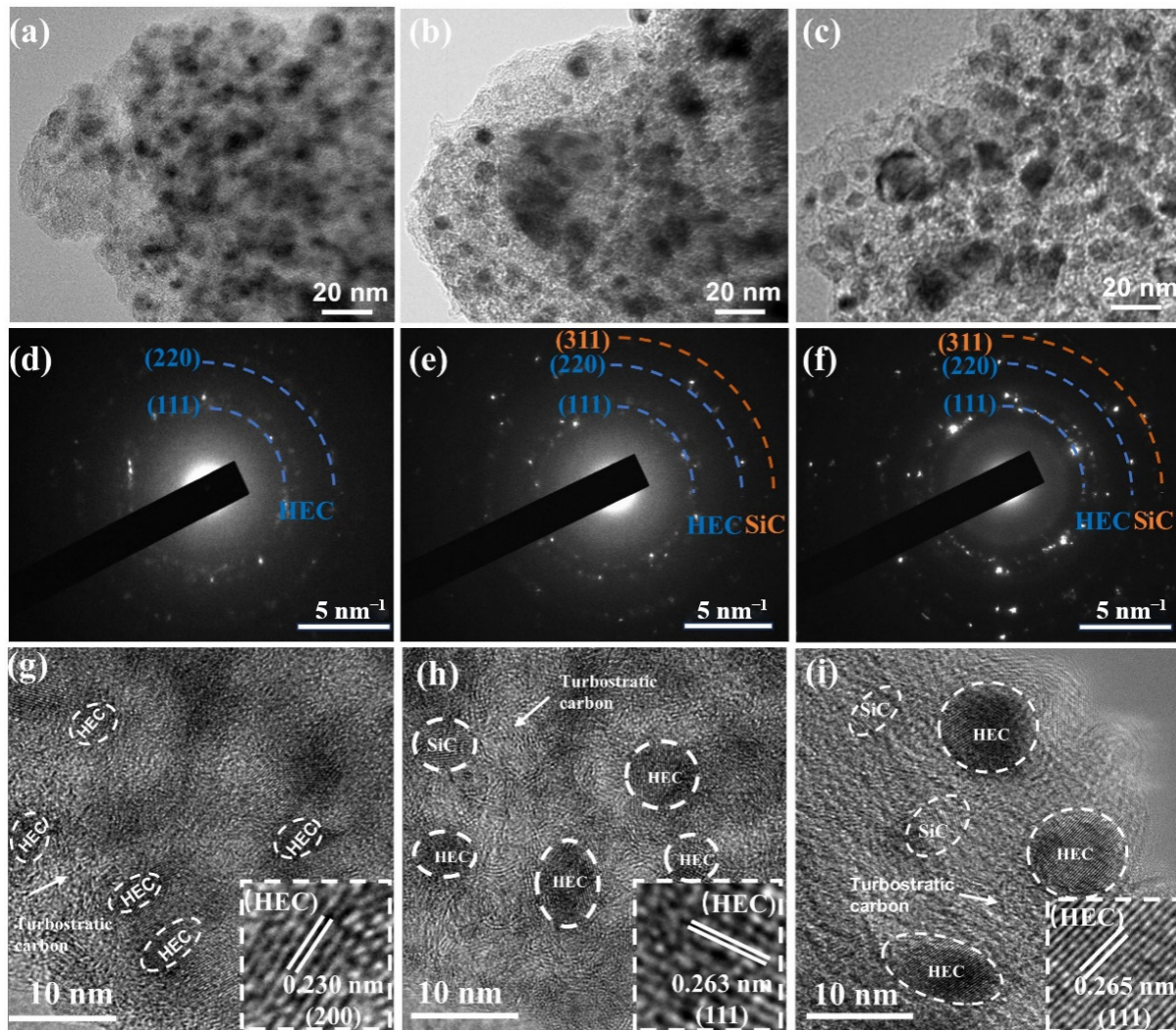


Fig. 7 (a–c) TEM images, (d–f) selected-area electron diffraction, and (g–i) HRTEM images of HEC/SiBCN-1 pyrolyzed at temperatures of (a, d, g) 1400 °C, (b, e, h) 1600 °C, and (c, f, i) 1800 °C.

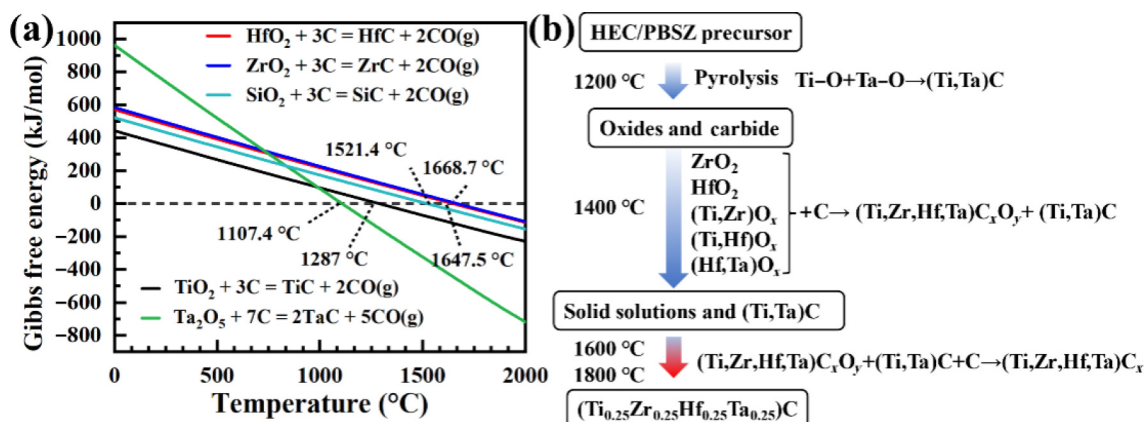


Fig. 8 (a) Gibbs free energy calculation of carbothermal reactions and (b) schematic diagram of formation of HEC/SiBCN ceramics and possible chemical reactions.

reaches 35 MPa, demonstrating their good load-bearing ability. In addition, some zig-zags can be observed at the initial stage in the local amplification diagram, similar to previously reported aerogels [15,40], which should be caused by pore collapse during the compression process or the extension of existing cracks under pressure. The high compressive strength achieved in the porous HEC/SiBCN ceramic should benefit from ultrafine and

homogeneous mesopores at the microscale in the ceramics. In addition, the bonding among the HEC/SiBCN nanoparticles could be increased by the crosslinking reactions of PBSZ, DVB, and HEC precursors during solvothermal reactions and by the bonding rearrangement of Si–C and Si–N [16] during the organic-to-inorganic transformation process to form a coarse skeleton, which may also favor the enhanced strength. Figure 9(c) shows

that our porous HEC/SiBCN ceramics display excellent compressive strength while maintaining extremely low thermal conductivity compared with the porous ceramics reported thus far, as listed in Table S4 in the ESM, indicating their great potential in current and future thermal insulating applications.

3.4 High-temperature stability of porous HEC/SiBCN ceramics

As the usage temperature of porous ceramics increases, it is critical to evaluate their thermal stability under high-temperature environments to ensure their reliability and safety. Here, the porous HEC/SiBCN ceramics were thermally treated at 1600 and 1800 °C for 2 h under argon, after which their structural evolution during the treatment and properties after treatment were studied to estimate their high-temperature stability. The pure porous SiBCN ceramics exhibit an obvious mass loss after thermal treatment in argon (3.7 wt% at 1600 °C and 10.5 wt% at 1800 °C), accompanied by a large linear shrinkage from 4.9% at 1600 °C to 6.8% at 1800 °C, as shown in Fig. 10(a). It is believed that the mass loss of the SiBCN ceramics during thermal treatment should be attributed to carbothermal reduction and decomposition of oxygen- or nitrogen-containing phases (e.g., $\text{SiO}_x\text{C}_{4-x}$ and $\text{SiC}_x\text{N}_{4-x}$) in the SiBCN matrix [15,37], further leading to the accumulation of internal stress and deterioration of the properties of SiBCN ceramics [16]. In addition, the high porosity (64.1%) of the SiBCN ceramics accelerates the atom diffusion and activity, facilitating carbothermal reduction and decomposition in the matrix, further causing obvious mass loss and shrinkage during treatment.

In contrast, for the HEC/SiBCN ceramics, the mass loss and linear shrinkage significantly reduce to lower levels after thermal treatment, as shown in Figs. 10(a) and 10(b). Specifically, the mass loss of HEC/SiBCN-0.5 is only 0.95% and 2.2%, accompanied by linear shrinkages of 2.5% and 3.3% after treatment at 1600 and 1800 °C, respectively, which are superior to pure SiBCN ceramics, indicating effective inhibition of the thermal decomposition of the SiBCN matrix. However, unexpectedly, the weight loss of the HEC/SiBCN ceramics increases with increasing HEC content during the thermal treatment. In our opinion, insufficient carbon in the precursor or pyrolyzed temperature/time may lead to insufficient carbothermal reduction during pyrolysis, resulting in small amounts of metal oxides remaining in the high-HEC-loading ceramics, further leading to increased mass loss during thermal treatment. Moreover, the densities of the treated HEC/SiBCN ceramics slightly increase compared with those of the as-prepared HEC/SiBCN ceramics but still maintain at a low level (0.74–1.12 g/cm³), as shown in Fig. 10(c). For example, the density of 1800 °C-treated HEC/SiBCN-0.5 is 0.92 g/cm³, which is just 0.05 g/cm³ greater than before. Therefore, compared with the

pure porous SiBCN ceramics, the porous HEC/SiBCN ceramic has superior thermal stability, which is closely related to the introduction of the HEC phase into the matrix.

The phase evolution of the porous HEC/SiBCN ceramics after thermal treatment was characterized by XRD in comparison with that of the pure SiBCN ceramics, as shown in Fig. 10(d) and 10(e). The treated SiBCN and HEC/SiBCN ceramics maintain the phase structure as before, but the diffraction peaks of the SiC and HEC phases correspondingly increase with increasing temperature from 1600 to 1800 °C, accompanied by an increase in the grain size (Fig. 10(f)), indicating continued phase separation and/or carbothermal reactions during the thermal treatment. Notably, the grain size of the SiC nanocrystals gradually decreases from 32 to 18 nm as the HEC content increases, while the HEC grains gradually increase from 9 to 13.5 nm, as shown in Fig. 10(f), illustrating that the formation of the HEC phase enhances the crystallization resistance of SiC phase in the SiBCN ceramics. SEM images (Figs. 10(g) and 10(h)) show that the treated HEC/SiBCN-1 maintains a three-dimensional porous network as before. Compared with Fig. 4(d), the nanoparticles and skeleton in the treated HEC/SiBCN-1 samples clearly coarsen, corresponding to sintering densification to a certain extent during treatment.

Figure 10(i) illustrates the changes in the thermal conductivity of the porous HEC/SiBCN ceramics with different HEC contents before and after the treatment. The increase in the thermal conductivity of pure SiBCN from 0.083 to 0.113 W/(m·K) after 1800 °C treatment may be attributed to decreased porosity and an increased SiC phase. Although the thermal conductivity of the porous HEC/SiBCN ceramics also increases after thermal treatment at 1800 °C, it still maintains at a low level of 0.067–0.082 W/(m·K). Furthermore, the increase in the thermal conductivity of the porous HEC/SiBCN ceramic greatly decreases with increasing HEC content (Fig. 10(i)), further indicating the beneficial effect of the HEC phase on the thermal stability of the SiBCN ceramics, which is consistent with our previous works [15]. The compressive strength of the HEC/SiBCN ceramics slightly decreases after treatment, indicating that the strength of HEC/SiBCN-0.5 remains at approximately 15 and 12 MPa after 1600 and 1800 °C treatments, respectively (Fig. S11 in the ESM). During the process of thermal treatment, the carbothermal reduction and decomposition of the oxygen- or nitrogen-containing phases (e.g., $\text{SiO}_x\text{C}_{4-x}$ and $\text{SiC}_x\text{N}_{4-x}$) in the SiBCN matrix undergo carbothermal reduction and decomposition with the release of gas, which could lead to the accumulation of internal stress and deterioration of mechanical properties [15,16]. Additionally, the grain growth of the SiC and HEC crystals during treatment also has a negative effect on the mechanical properties of the HEC/SiBCN ceramics.

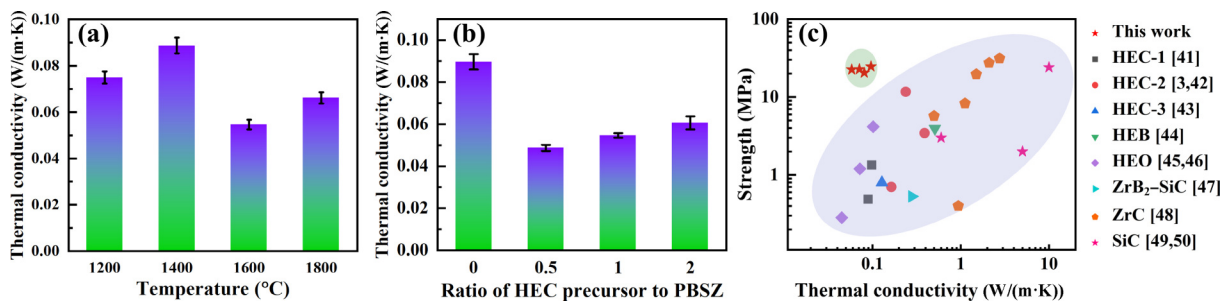


Fig. 9 Thermal insulation of porous HEC/SiBCN ceramics: (a) HEC/SiBCN-1 pyrolyzed at different temperatures and (b) HEC/SiBCN ceramics with different HEC contents pyrolyzed at 1600 °C; (c) thermal conductivity vs. compressive strength of HEC/SiBCN ceramics compared with other porous ceramics [3,41–50].

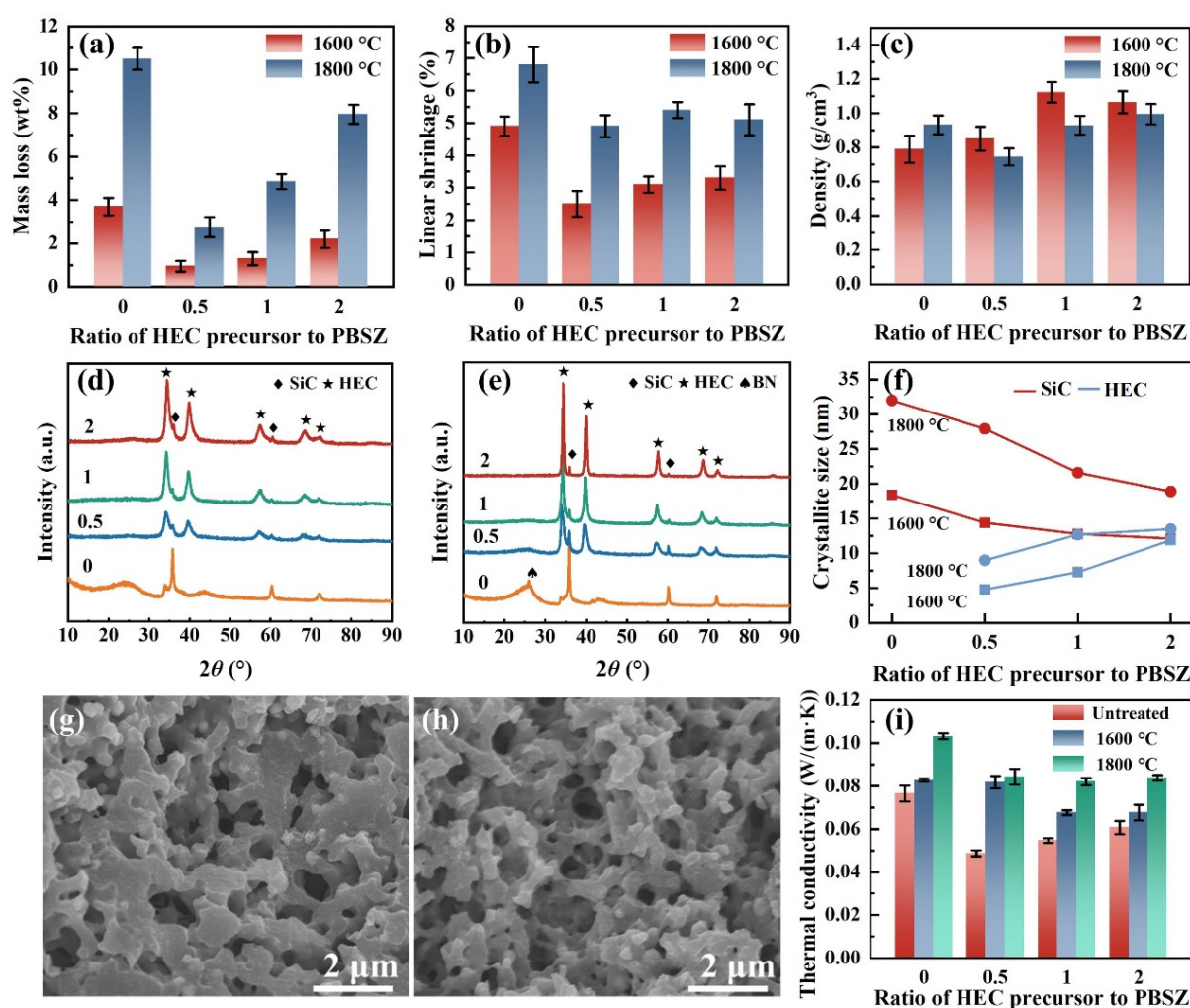


Fig. 10 High-temperature stability of 1600 °C-pyrolyzed porous HEC/SiBCN ceramics after thermal treatment at 1600 and 1800 °C in an argon atmosphere for 2 h: (a) mass loss, (b) linear shrinkage, (c) density, XRD patterns after thermal treatment at (d) 1600 and (e) 1800 °C, and corresponding (f) crystallite sizes of SiC and HEC phases, SEM images of HEC/SiBCN-1 after thermal treatment at (g) 1600 °C and (h) 1800 °C, and (i) thermal conductivity of HEC/SiBCN ceramics after thermal treatment.

4 Conclusions

In summary, porous HEC/SiBCN ceramics, which possess high porosity, low thermal conductivity, and excellent compressive strength, were successfully fabricated from multi-metal-containing PBSZ precursors. The HEC phase of $(\text{Ti}_{0.25}\text{Zr}_{0.25}\text{Hf}_{0.25}\text{Ta}_{0.25})\text{C}$ is formed *in situ* by carbothermal reduction of the HEC precursor with highly active free carbon in the SiBCN matrix at a relatively low temperature of 1600 °C. Various metal oxides initially form and then transform into metal carbides by carbothermal reduction, followed by the formation of multicomponent solid solution of metal carbides at elevated temperatures. Importantly, the formation of the stable HEC phase preferentially consumes free carbon in the SiBCN matrix, thus hindering the crystallization and growth of the SiC phase in high-temperature environments, which endows the porous HEC/SiBCN ceramics with excellent thermal stability up to 1800 °C under argon. This work provides a strategy for constructing an HEC phase *in situ* into a porous SiBCN matrix to enhance the overall performance, which will extend its application in harsh environments.

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Declaration of competing interest

The authors have no competing interests to declare that are relevant to the content of this article.

Electronic Supplementary Material

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