

Low temperature synthesis nanoscale Ta₄HfC₅ powder and characterization of Ta₄HfC₅ ceramics

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Research Article

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Abstract

Solvothermal treatment was used to synthesize nanoscale Ta₄HfC₅ powder at a relatively low calcination temperature (1400 °C) and in a short period through material selection and process optimization. High-volume Teflon-lined stainless steel autoclave (1000–2000 mL) could be used to prepare powder by using this method. The obtained powder had good size distribution and dispersity. Ta₄HfC₅ powder could be obtained at a low temperature because of the existence of Ta₂Hf₆O₁₇ during carbothermal reduction. Ta₄HfC₅ ceramics were consolidated via spark plasma sintering at 2100 °C and at 30, 40, and 50 MPa. Holding time was 5 min. Ceramics had a better densification and smaller grain sizes at a shorter sintering time compared with that of the mechanical ball milling method. The densification behavior of ceramics was analyzed, and the mechanical properties of different samples were investigated. Flexural strength increased from 5.85 ± 0.43 GPa to 10.07 ± 0.61 GPa. Fracture toughness was similar in all the compositions in the range of 2.36–2.56 MPa m^{1/2}. This method can be applied to synthesize Ta₄HfC₅ powder with high purity and uniformity in large quantities. Hence, ceramic sintering and Ta₄HfC₅–matrix composite preparation have a broad application prospect.

1. Introduction

Carbides from transition metal groups IVB and VB have high melting points (above 3000 °C)^[1]. These carbides have important applications for spacecraft structures, such as rocket nozzles, wing leading edges, and nose caps. For these carbides, TaC and HfC possess high melting point (3800 °C–3900 °C), high elastic modulus (400–500 GPa), high hardness (15–20 GPa), and moderate thermal expansion coefficient^[2-5]. TaC and HfC are NaCl-type structures and thus can form unlimited solid solutions Ta_xHf_{1-x}C^[6]. In this system, the highest melting point of Ta₄HfC₅ is 3942 °C^[7], which provides feasibility for aircrafts to work in a higher environmental temperature.

Raw TaC and HfC powders have been milled to synthesize Ta₄HfC₅ because of their NaCl-type structure. However, this method has obvious defects. With mechanical ball milling, powders can be just mixed sufficiently, but a single-phase Ta₄HfC₅ solid solution cannot be obtained because of the high covalent bonds and low self-diffusion coefficients of TaC and HfC^[8,9]. Hot pressing or spark plasma sintering should be used to promote the formation of Ta₄HfC₅ ceramic, not Ta₄HfC₅ powder. However, the ceramic needs to be broken again and takes a long time to mill to obtain powders. Sintering temperature is normally above 2000 °C, which makes particle sizes nonuniform from several microns to tens of microns^[10]. In some works, sintering aids, such as MoSi₂^[11], B₄C^[12], and TaB₂^[13], have been added to reduce sintering temperature and control grain sizes. However, these methods cannot guarantee the purity of Ta₄HfC₅. In addition, mechanical ball milling can hardly synthesize superfine powder. These greatly limit the application field of the Ta–Hf–C system.

Few articles on the preparation of Ta₄HfC₅ powder via chemical methods have been published. However, there is still possibility of improvement such as reducing calcination temperature, simplifying raw

material treatment and reducing drying time^[14-16].

This work aimed to synthesize a polymer precursor for Ta₄HfC₅ powder through material selection and process optimization, which could shorten the preparation period and obtain Ta₄HfC₅ powder at a lower calcination temperature. Particle size uniformity becomes uncontrollable as the volume of the steel autoclave increases; however, this method could be conducted in 2000 mL Teflon-lined stainless steel autoclave to prepare Ta₄HfC₅ powder with high yield, particle sizes, and dispersity that were similar to those prepared in a 100 mL autoclave.

Ta₄HfC₅ ceramics sintered via spark plasma sintering had a higher relative density at a shorter sintering time compared with that of ceramics sintered through mechanical ball milling method. The mechanical properties of ceramics were investigated, and their densification behaviors were analyzed.

2. experimental Procedure

2.1 Raw materials

Tantalum pentachloride (TaCl₅) and hafnium chloride (HfCl₄), which were 99.9 wt.% in purity, were purchased from J&K Chemicals Superfine Materials Co., Ltd., Hebei, China. TaCl₅, HfCl₄, N-butyl alcohol, and acetylacetone (AcAc) were used to prepare tantalum hafnium precursors. Phenolic resin (THC-400; Shanxi Taihang Impedefire Polymer Limited Company, Shanxi, China) was used as a carbon source.

2.2 Powder preparation

HfCl₄ was dissolved in acetylacetone and added with N-butyl alcohol and a stoichiometric amount of TaCl₅. After 1 h, a stoichiometric amount of phenolic resin was blended in and stirred for 1–1.5 h. An additional 3 wt.% phenolic resin was added to inhibit the oxidation of the powder surface and avoid oxygen residue during the reaction. The whole process was stirred in an oil bath. After stirring was finished, the mixture was transferred into a Teflon-lined stainless steel autoclave and autoclaved at 200 °C for 12 h. Then, the mixture was dried at 120 °C to obtain the Ta₄HfC₅ precursor, which was calcined at 1400 °C for 2 h with a heating rate of 5 °C/min under an argon flow. Then, the furnace was cooled to 400 °C at the same rate of 5 °C/min and then naturally cooled to room temperature. The precursors were calcined at 1000 °C, 1100 °C, 1200 °C, 1300 °C, and 1400 °C to study the carbon thermal reduction of Ta₄HfC₅ precursor at different calcination temperatures.

2.3 Spark plasma sintering

Ta₄HfC₅ powder was sintered through a spark plasma sintering machine. The powder was placed in a 40 mm-diameter graphite die wrapped with graphite foil. The powder was first loaded to the required uniaxial pressure, and the vacuum was pumped and began to heat up.

The heating rate before 500 °C was 50 °C/min, and the heating rate from 500 °C to 2100 °C was 100 °C/min. The uniaxial pressures were 30, 40, and 50 MPa. The holding times were 5 min and cooling with a furnace. The environment in the vacuum was set at a pressure of 2 Pa.

2.4 Characterization

X-ray powder diffractometer (XRD, X'PERT PRO MPD, Holland) using CuK α radiation (40 kV, 30 mA) and X-ray photoelectron spectroscopy (XPS, Escalab 250, USA) were employed to analyze the phase composition of the samples. The morphological characteristics of Ta₄HfC₅ powder and Ta₄HfC₅ ceramics were investigated with a scanning electron microscope (SEM, HELIOS NanoLab 600i, USA). Fourier-transform infrared (FTIR) spectroscopy was conducted to analyze the chemical structure of Ta₄HfC₅ precursor by using an Avatar 380 (Thermo Fisher, USA). Flexural strength was tested in three-point bending, and the sample size was 3 mm × 4 mm × 36 mm by using a 30 mm span and a crosshead speed of 0.5 mm/min (AG-X Plus 20 kN/5 kN, Japan). Fracture toughness was investigated via the single-edge notched beam method. The samples were 2 mm × 4 mm × 22 mm with a 16 mm span and a crosshead speed of 0.05 mm/min (AG-X Plus 20 kN/5 kN, Japan).

3. Results And Discussion

3.1 Characterization of Ta₄HfC₅ powder

Fig. 1 shows the XRD patterns of Ta₄HfC₅ powder calcined from 1000 °C to 1400 °C. The characteristic peaks were mainly Ta₂O₅ and TaC when the temperature was heated to 1000 °C. Ta₂Hf₆O₁₇ began to appear between 1000 °C and 1200 °C. After 1200 °C, only hafnium oxides existed in Ta₄HfC₅ precursor. These hafnium oxides had two different crystal structures: monoclinic HfO₂ and orthorhombic HfO₂. No other peaks existed as the temperature increased to 1400 °C. The precursor was completely converted to Ta₄HfC₅ powder. Orthogonal HfO₂ completely reacted before 1300 °C, but monoclinic HfO₂ needed 1300 °C.

Fig. 1 XRD patterns of powder calcined from 1000 °C to 1400 °C

Ta₄HfC₅ powder can be prepared at 1400 °C, which below 1600 °C for other works^[14,15]. For the Hf–O–C system, the preparation temperature of HfC is generally higher than 1600 °C^[17], which limited the formation of Ta₄HfC₅ powder at a lower temperature. The precursor is converted to Ta₂Hf₆O₁₇ at 1100 °C instead of independent Ta₂O₅ and HfO₂^[15]. Converting Ta–O–Hf to Ta–Hf–C took lesser energy than converting Ta–O and Hf–O to Ta–Hf–C.

Ta₄HfC₅ powder was investigated through SEM analysis as shown in Fig. 2. The powder presented good uniformity and dispersion at lower magnification (Fig. 2a). The small amount of agglomeration shown in the figures was the agglomeration of the precursor during drying and could be refined by grinding. Fig. 2(b) presents that the particle size of Ta₄HfC₅ powder was nanoscale. Figs. 2(c)–(e) show the

homogeneous distribution of the different elements as observed via energy-dispersive X-ray spectroscopy, which had over 3000 scan points to ensure the accuracy of the result. Ta and Hf were distributed uniformly. This method solved the problem of the uneven distribution of Ta and Hf when Ta₄HfC₅ powder was prepared via mechanical ball milling method.

Fig. 2 Morphological characteristics and elemental distribution of Ta₄HfC₅ powder

Fig. 3 shows the XPS spectrum of Ta₄HfC₅ powder prepared at 1400 °C. The identified peaks at 12.98 eV and 14.68 eV are assigned to Hf–C bonds, and the peaks at 15.53 eV and 17.18 eV correspond to Hf–O bonds. Fig. 3(b) shows the spectrum of Ta4f, which reveals Ta–C bonds at 21.73 eV and 23.63 eV and Ta–O bonds at 24.43 eV and 26.13 eV, respectively. No obvious peaks of tantalum oxide or hafnium oxide were observed in the XRD pattern in Fig. 1; therefore, the Hf-O and Ta-O bonds might be derived from contamination during testing rather than the presence of oxides in the powder itself

Fig. 3 X-ray photoelectron spectrum of Ta₄HfC₅ powder

Fig. 4 shows the FTIR spectrum of the Ta₄HfC₅ precursor. Ta–O–Hf precursor without phenolic resin was prepared through the same process as a reference to analyze the changes in the chemical structure during precursor synthesis. The absorption peak of O–H near 3420 cm⁻¹ showed that associated and free hydroxyl groups existed in the system and indirectly indicated that O–H was connected with multiple metal atoms.

The absorption peaks near 2960 cm⁻¹ and 2851 cm⁻¹ corresponded to the absorption peak of C–H in –CH₂ and –CH₃, respectively. After phenolic resin was added, a C=C stretching vibration near 1540 cm⁻¹ appeared, and the vibration absorption peak of C=O stretching vibration corresponding to ketone appeared at about 1578 cm⁻¹. These two peaks were the characteristic peaks of Ta(AcAc)_x and Hf(AcAc)_x, which corresponded to the C=C and C=O stretching vibration in the enol-type structure.

The absorption peak near 1127 cm⁻¹ weakened and disappeared after phenolic resin was added, but peaks appeared at 1164 cm⁻¹, 1113 cm⁻¹, and 1051 cm⁻¹, which were C–O stretching vibrations. Combined with the spectra of phenolic resin, this peak might be the weak absorption peak caused by Ta–O–C and Hf–O–C.

Fig. 4 FTIR of phenolic resin, Ta–O–Hf precursor, and Ta₄HfC₅ precursor

3.2 Characterization of Ta₄HfC₅ ceramics

Table 2 shows the relative density of Ta₄HfC₅ ceramics. The relative density of the ceramic sintered at 2100 °C for 5 min at 30 MPa was 81.61%. This result was better than the relative density of Ta₄HfC₅ ceramics sintered through mechanical ball milling at 2050 °C for 20 min at 32 MPa, which was 77.9% [10].

The relative density increased to 88.60% when uniaxial pressure increased to 50 MPa. Densification behavior is discussed in detail later in this article.

Fig. 5 Fractured surfaces of Ta₄HfC₅ ceramics at different uniaxial pressures:

(a) 30 MPa, (b) 40 MPa and (c) 50 MPa

Fig. 5 shows the SEM images of the fractured surfaces of all Ta₄HfC₅ ceramics. The fracture morphology at 30 MPa was basically granular agglomeration, sintering phenomenon was hardly observed. At 40 MPa, grain size increased, whereas porosity decreased, but agglomeration could still be observed. Sintered neck was observed when uniaxial pressure increased to 50 MPa. The agglomeration of powder basically disappeared.

The grain sizes of the ceramic did not increase too much and still had good uniformity compared with the initial Ta₄HfC₅ powders. This result was obviously superior to Ta₄HfC₅ ceramics sintered via mechanical ball milling.

Table 1 shows the mechanical properties of Ta₄HfC₅ ceramics sintered under different uniaxial pressures. The increase in relative density could obviously improve the hardness of ceramics and flexural strength, The hardness increased from 5.85 ± 0.43 GPa to 10.07 ± 0.61 GPa at the same holding time. Flexural strength increased from 5.85 ± 0.43 GPa to 10.07 ± 0.61 GPa, but it slightly affected fracture toughness. The fracture toughness for all compositions were similar in the range of 2.36–2.56 MPa m^{1/2}.

Table 1 Relative density and mechanical properties of Ta₄HfC₅ ceramics

Sintering Conditions °C/MPa/min	Relative density %	Mechanical properties		
		<i>Hv</i> (GPa)	<i>K_{IC}</i> (MPa·m ^{1/2})	<i>σ</i> (MPa)
2100/30/5	81.61	5.85 ± 0.43	2.36 ± 0.06	119.94 ± 5.21
2100/40/5	83.27	6.64 ± 0.48	2.40 ± 0.14	151.76 ± 11.3
2100/50/5	88.60	10.07 ± 0.61	2.56 ± 0.12	244.21 ± 10.4

3.3 Densification behavior of Ta₄HfC₅ ceramics

Fig. 6 shows the sintering curves of Ta₄HfC₅ ceramics sintered via spark plasma sintering under different uniaxial pressures. All the densification rates showed negative growth before 500 °C. The part of gas between particles would expand as temperature increased and would discharge slowly from the gap between mold and punches. Hence, a slower heating rate was applied before 500 °C because a rapid

heating rate at the beginning would cause the gas instantly expand and generate local high pressure, which would quickly overflow powder from the gap, even directly destroy the mold.

All the powders started shrinking from 600 °C to 2100 °C because of the partial sintering of ceramics and the exhaustion of gas at a higher temperature. The gas in the pores produced spark discharge, generated ionization, and released a large amount of plasma, thereby promoting sintering densification. The maximum shrinking rates as the uniaxial pressure increased were 2.13×10^{-3} , 4.45×10^{-3} , and 2.35×10^{-2} mm/s at 30, 40, and 50 MPa, respectively.

Fig. 6 Sintering curves of Ta₄HfC₅ ceramics under different uniaxial pressures:

(a) 30, (b) 40, and (c) 50 MPa

The sintering displacement curves of the three ceramics still increased slowly at 2100 °C when sintering temperature was constant. This finding indicated that relative density would continue to increase with the extension of the constant sintering time. If the sintering time was long enough, nearly full-dense Ta₄HfC₅ ceramics might be theoretically obtained.

In addition, the high-speed moving plasma hit the surface of the particles, which would eliminate the oxides on surface and make it easier to purify and activate. We added additional phenolic resin before to make it possible to remove the oxides, which was beneficial to further increase the densification of ceramics.

For the densification behavior of Ta₄HfC₅ ceramics, fully dense Ta₄HfC₅ ceramic was difficult to sinter at approximately 2000 °C and would need a higher uniaxial pressure because of the numerous covalent bonds and high melting points of the Ta–Hf–C system. Some pores were inevitably left during the shorter sintering time because of low self-diffusion coefficients and small liquid phase filling. Nanoscale particles had a higher sintering activity; however, their relative density was still higher than that sintered through mechanical ball milling under similar conditions.

Although spark plasma sintering had the advantages of the faster heating rate and shorter sintering time, no obvious advantages were observed when sintering Ta–Hf–C ceramics at around 2000 °C. In some works, TaC/TaC–HfC ceramics are sintered without sintering additives, and the relative density is over 90%. However, most works have used hot pressing, which involves longer time, higher temperature, or higher pressure^[18,20,21]. However the ultrafine powder is still difficult to obtain full densification ceramic via hot pressing^[22]. Ta–Hf–C ceramics sintered through spark plasma sintering can also achieve a higher densification in a shorter time but will require a higher sintering temperature than hot pressing^[10].

Conclusion

Ta₄HfC₅ powder was prepared at a lower temperature (1400 °C) and in a shorter period through raw material selection and process optimization. The process was simple and could be used to prepare

nanoscale Ta₄HfC₅ powder in a high-volume autoclave. Particle size distribution was not affected by the change in the size of autoclaves, and the powder had good size distribution and dispersity. The product and structural changes in the precursor in carbon thermal reduction were studied. Ta₂Hf₆O₁₇ was generated at 1100 °C; therefore, the formation of Ta₄HfC₅ powder at a lower temperature was feasible. Ta₄HfC₅ ceramics were sintered via spark plasma sintering and had better densification and smaller grain sizes compared with the ceramics sintered through mechanical ball milling method under similar sintering conditions.

Declarations

Acknowledgments

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Figures

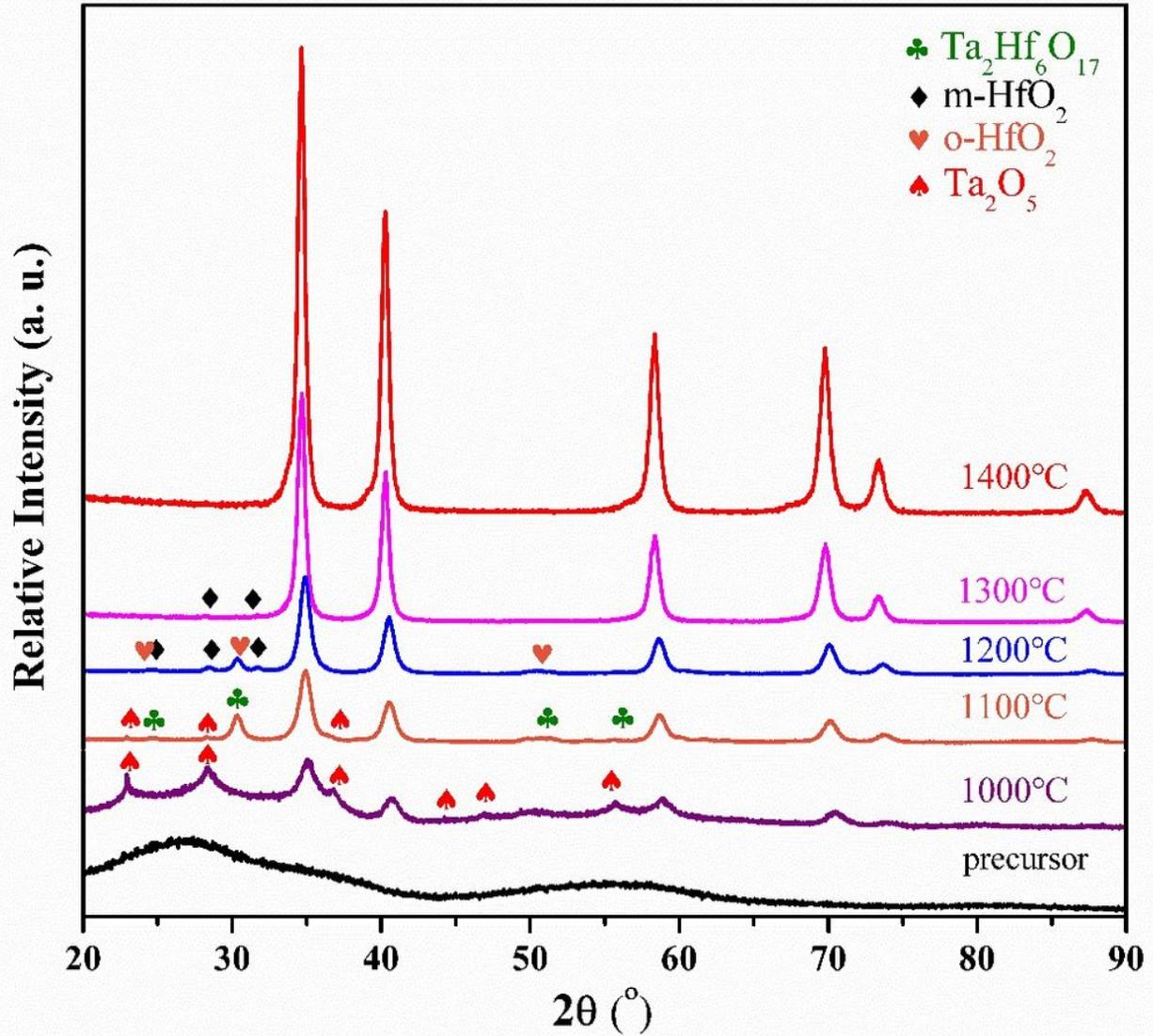


Figure 1

XRD patterns of powder calcined from 1000 °C to 1400 °C Ta₄HfC₅ powder can be prepared at 1400 °C, which is below 1600 °C for other works [14,15]. For the Hf–O–C system, the preparation temperature of HfC is generally higher than 1600 °C [17], which limited the formation of Ta₄HfC₅ powder at a lower temperature. The precursor is converted to Ta₂Hf₆O₁₇ at 1100 °C instead of independent Ta₂O₅ and HfO₂ [15]. Converting Ta–O–Hf to Ta–Hf–C took less energy than converting Ta–O and Hf–O to Ta–Hf–C.

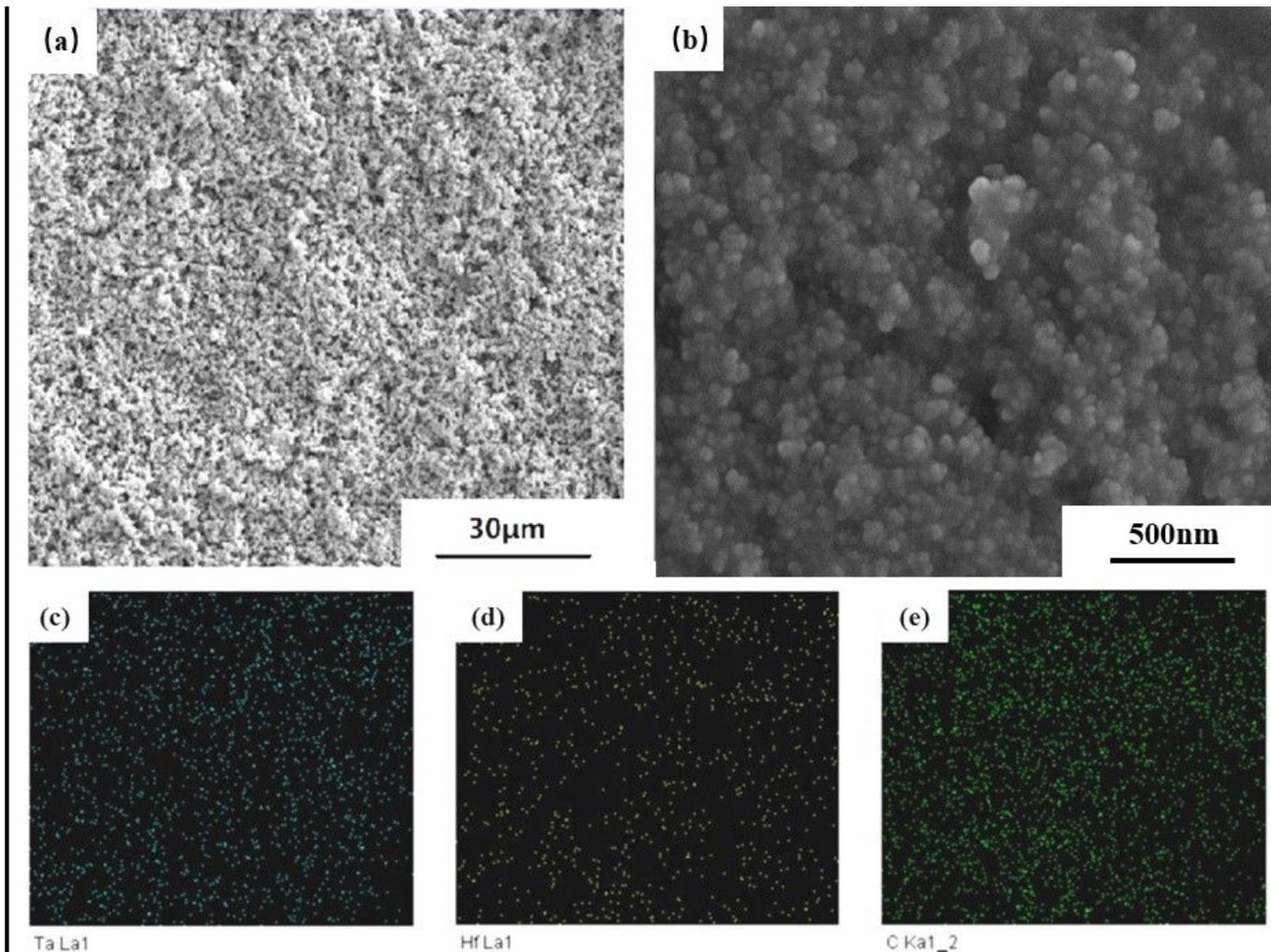


Figure 2

Morphological characteristics and elemental distribution of Ta₄HfC₅ powder

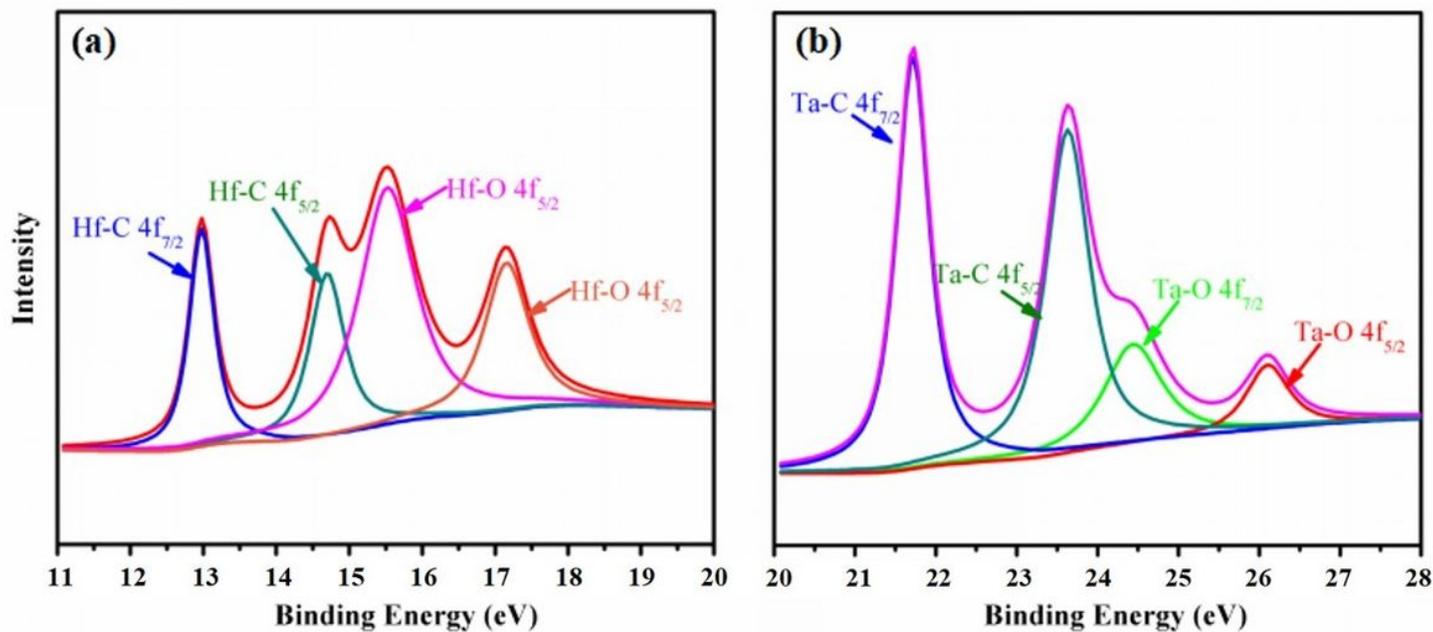


Figure 3

X-ray photoelectron spectrum of Ta₄HfC₅ powder

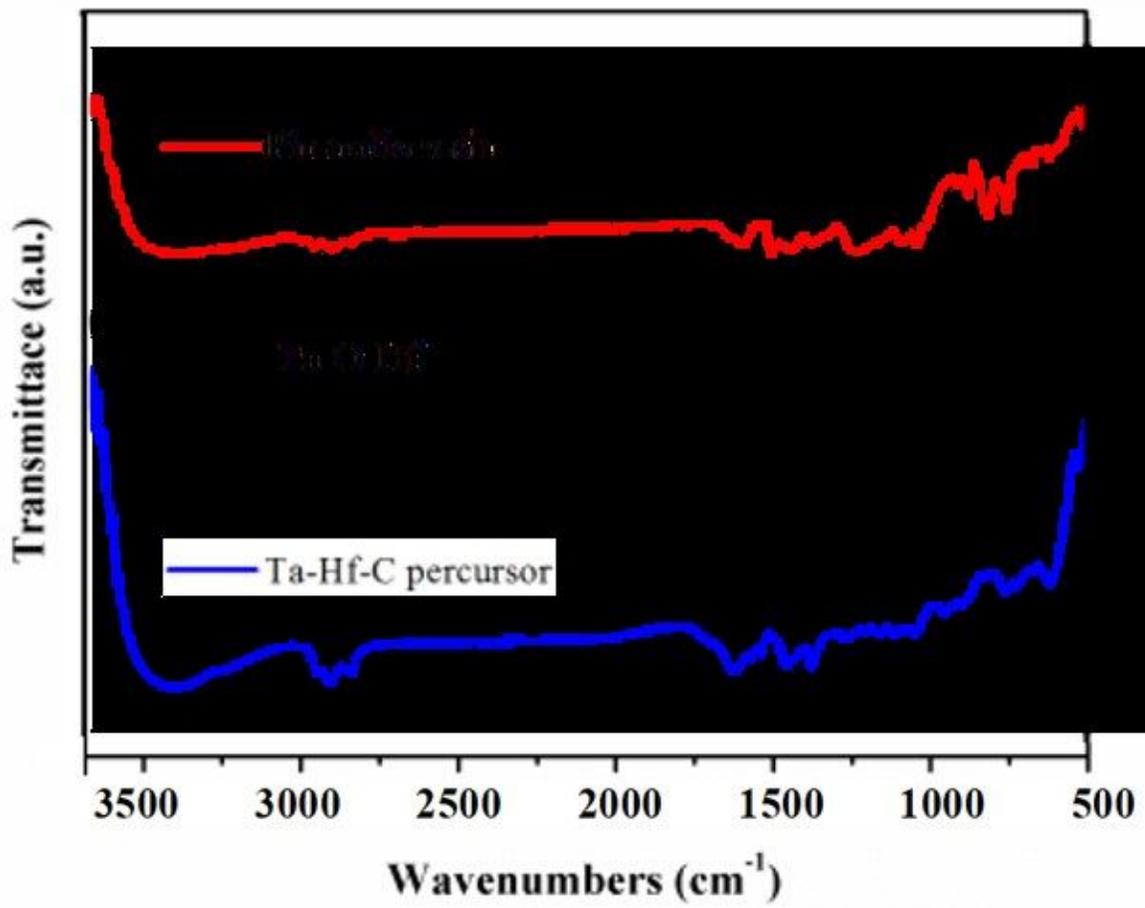


Figure 4

FTIR of phenolic resin, Ta-O-Hf precursor, and Ta₄HfC₅ precursor

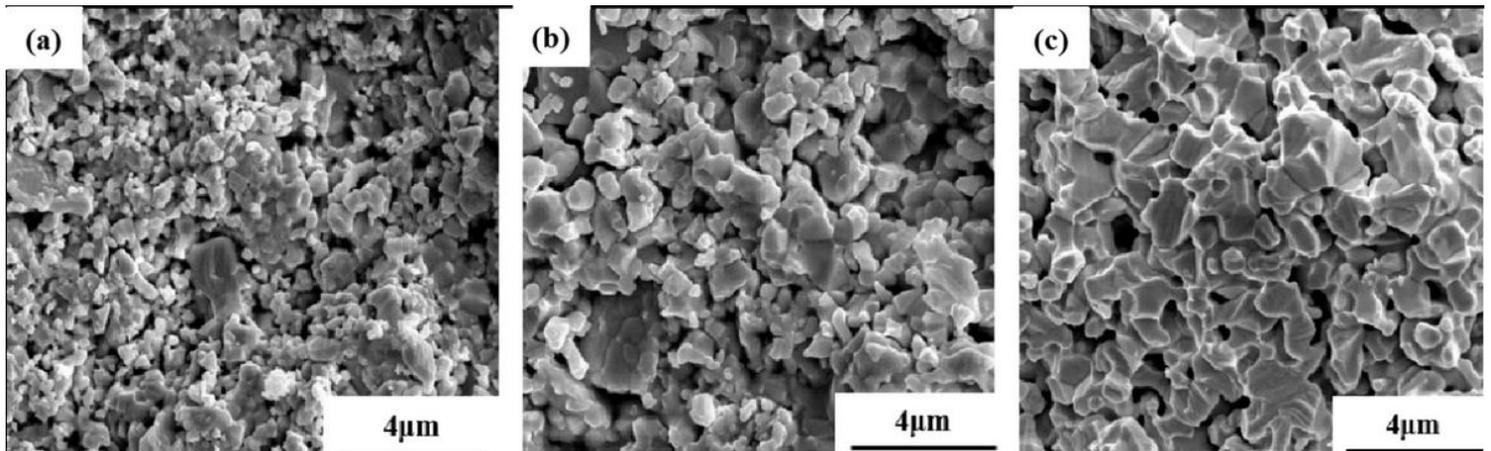


Figure 5

Fractured surfaces of Ta₄HfC₅ ceramics at different uniaxial pressures: (a) 30 MPa, (b) 40 MPa and (c) 50 MPa

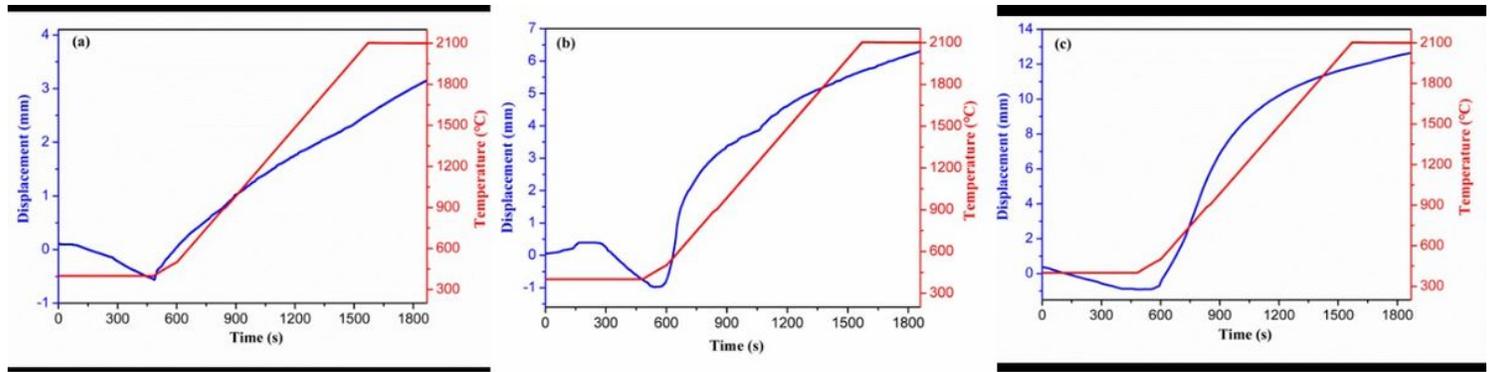


Figure 6

Sintering curves of Ta₄HfC₅ ceramics under different uniaxial pressures: (a) 30, (b) 40, and (c) 50 MPa