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Synthesis, Ceramic Conversion and Microstructure Analysis of TaC-SiC Ceramics by Hybrid Precursor Route

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Abstract: The synthesis and characterization of nano-tantalopolycarbosilanes (TS) and their transformation into ceramic materials were reported. The TS-5, TS-10, TS-25, and TS-55 hybrid precursors were prepared using nanometer tantalum powders (nano-Ta) and polycarbosilane (PCS), according to the quality of tantalum powders 5 wt%, 10 wt%, 25 wt%, 55 wt%, via a ultrasonic and ball mill mixing method. The composition, structure, uniformity and pyrolysis process of the obtained precursors were investigated by infrared (IR), thermogravimetric (TGA), element analysis, SEM characterization, and so on. The results show that nano-Ta is dispersed uniformly in PCS. The ceramic yield of the precursors increases gradually with the increase of nano-Ta proportion. The inorganic conversion is almost completed at 1073 K and TaC crystal appears, and nano-Ta is completely converted into TaC at 1673 K. As the temperature increases, the crystallization of TaC is sharper and sharper, which indicates the growth of TaC grain. The non-oxygen structure, high ceramic yield, and uniform composition enable the as-received hybrid precursor as promising materials to prepare high performance ultrahigh-temperature ceramics.

Key words: ultrahigh-temperature ceramics (UHTCs); hybrid precursor; TaC-SiC; powders

Refractory metal carbides, as members of ultrahigh-temperature ceramics (UHTCs), have received more and more attention due to their unusual combinations of physical and chemical properties[1-3]. Among these carbides, tantalum carbide (TaC) is characterized by high melting point (4256 K), high modulus (537 GPa), high hardness (15~19 GPa) and excellent corrosion resistance, and good resistance to chemical attack and thermal shock[4-6]. The excellent properties promise TaC as a candidate material for high-temperature applications. However, there are some restrictions for aerospace application such as poor oxidation resistance at high temperatures (873~1273 K) and low fracture toughness[7,8]. Fortunately, addition of second phases such as SiC and $MoSi_2$ has been proved to improve those properties[9,10].

Carbides have been synthesized by various methods[11,12]. The usual preparation method of TaC is precursor-derived ceramics method[13]. It is just simply reported that TaC-SiC ceramics were prepared via a hybrid-precursor-derived ceramics method using tantalum powders and nicalon polycarbonsilane[14], and the ceramic conversion and microstructure analysis of the ceramics were not repeated openly.

In this paper, TaC-SiC ceramics have been synthesized via pyrolysis of nanometer tantalum powders (nano-Ta) and polycarbonsilane (PCS). The composition, structure, uniformity and pyrolysis process of the obtained precursors were investigated.

1 Experiment

Nanometer tantalum powders (d=~50 nm) used as tantalum source were purchased from Beijing Deco Island Gold Technology Co., Ltd in Beijing, China. PCS (Mn=1720, Mw/Mn=1.7) was obtained from National University of Defense Technology in Hunan, China.

Synthesis of nano-tantalopolycarbosilanes (TS): Firstly, the nano-Ta were prepared according to the quality of nano-Ta 5 wt%, 10 wt%, 25 wt%, 55 wt%. Secondly, nano-Ta and PCS were dispersed in xylene solvent via a ultrasonic and ball mill mixing method. Thirdly, the mixtures were concentrated to obtain the TS-5, TS-10, TS-25, and TS-55 hybrid precursors.

Heat treatment of the hybrid precursors: The precursors were put in a graphite crucible. The crucible was placed into a furnace, which was heated in nitrogen atmosphere to 873 K and held at the temperature for 1 h. Additional heat treatments for the as-obtained ceramics were carried out in inert atmosphere in graphite furnace heated to 1073, 1273, 1473, 1673, 1873, 2273 K and held for an additional 1 h, to investigate the phase evolution.

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2 Result and Discussion

2.1 Microstructure of the hybrid precursors

SEM was introduced to characterize the microstructures of TS-5, TS-10, TS-25, and TS-55 hybrid precursors and the results are shown in Fig.1. It reveals that nano-Ta is dispersed uniformly into the PCS, though it can be seen that the surface of TS-55 hybrid precursor shows few small lumps (Fig.1d), which should be attributed to cluster of nano-Ta. It indicates that these hybrid precursors with uniform distribution can be prepared by blending nano-Ta and PCS via the ultrasonic and ball mill mixing method.

2.2 Heat treatment of the hybrid precursors

To understand the thermal behavior during the pyrolysis of the hybrid precursors, TGA was measured. As shown in Fig.2, the thermal decomposition, started at 633 K and ended at about 1073 K, is due to the evolution of volatile gases CH_3CH_3, SiH_4 and CH_3SiH_3[10]. It can be seen from Fig.2 and Table 1 that the ceramic yield of PCS, TS-5, TS-10, TS-25 and TS-55 reaches 61.75 wt%, 70.26 wt%, 71.92 wt%, 75.18 wt% and 87.96 wt%, respectively, when the hybrid precursors were heated to 1173 K. It indicates that the ceramic yield increases with the increase of nano-Ta. Meanwhile, the yield of hybrid precursor is higher than the calculated yield (Table 1), which indicates that the excess yield should result from the catalysis of nano-Ta, *i.e.* the evolution of these volatile gases is inhibited via further cross-linking accelerated by nano-Ta in the TS hybrid precursors.

Subsequently, in order to understand the structural evolution during the pyrolysis of the TS-25 hybrid precursor, FTIR was measured (Fig.3). From the spectra (Fig.3a and 3b), it can be seen that there is no obvious difference, which suggests that nano-Ta is introduced via physical blend without changing the structure of the PCS. At 873 K (Fig.3c), the absorption of Si-CH_3 at 1250 cm^{-1} and Si-H at 2100 cm^{-1} significantly decreases, which should be due to the decomposition of organic side groups. In the FTIR spectrum at 1073 K (Fig.3d), the broad absorption of SiC_4 at about 780 cm^{-1} is still retained, while the peaks attributed to organic groups such as Si-H, Si-CH_3 and Si-CH_2-Si could not be observed. It is believed

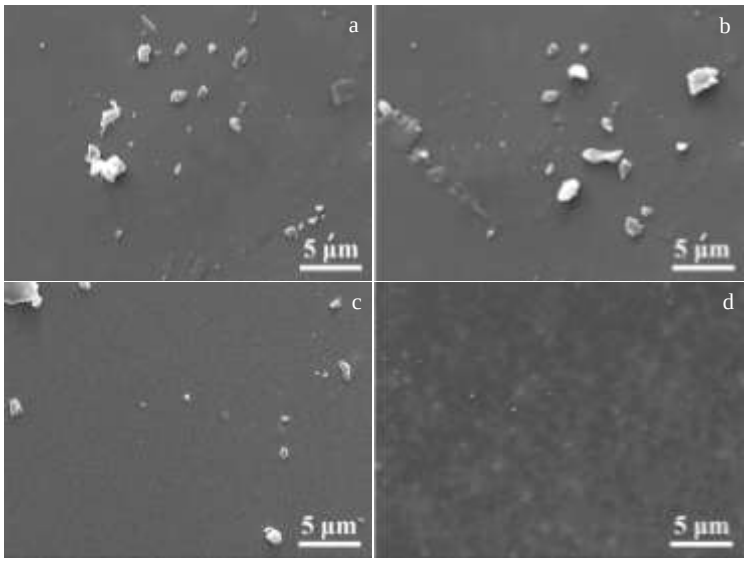

Fig.1 SEM images of TS-5 (a), TS-10 (b), TS-25 (c), and TS-55 (d)

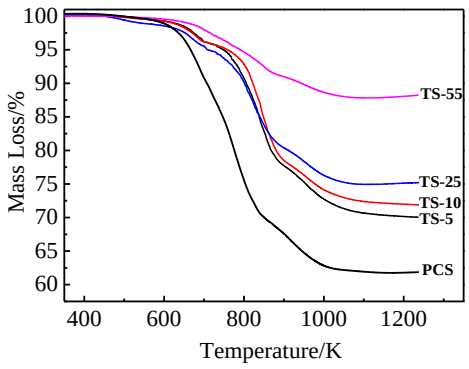

Fig.2 TGA curves of PCS and TS precursors in flowing nitrogen

Table 1 Ceramic yield of PCS, TS-5, TS-10, TS-25 and TS-55

Samples	Yield/wt%	Calculated yield[a]/wt%
PCS	61.75	-
TS-5	70.26	63.66
TS-10	71.92	65.58
TS-25	75.18	71.31
TS-55	87.96	82.79

Note: [a] Calculated yield is calculated based on the assumption that the yield is just the addition of that of PCS and nano-Ta

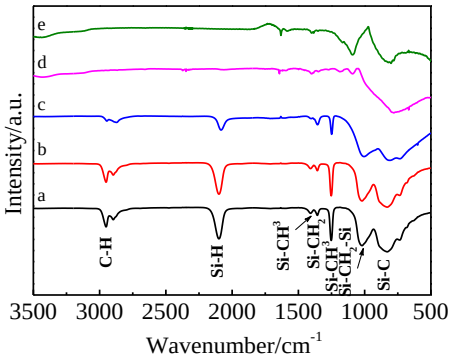

Fig.3 FTIR spectra of original PCS (a), TS-25 (b) and TS-25 precursor heat-treated at different temperatures: (c) 873 K, (d) 1073 K, and (e) 1673 K

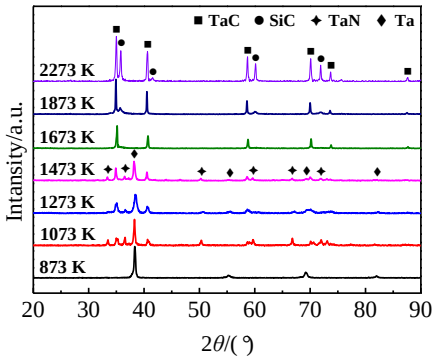

Fig.4 XRD patterns of ceramics derived from TS-25 at different temperatures

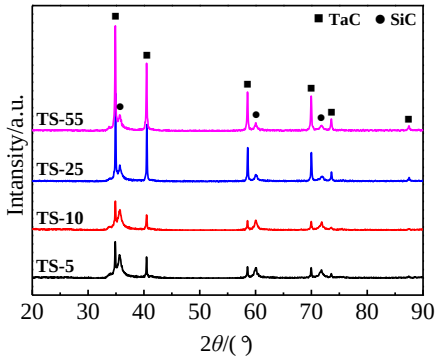

Fig.5 XRD patterns of ceramics derived from TS-5, TS-10, TS-25 and TS-55 hybrid precursors at 1873 K

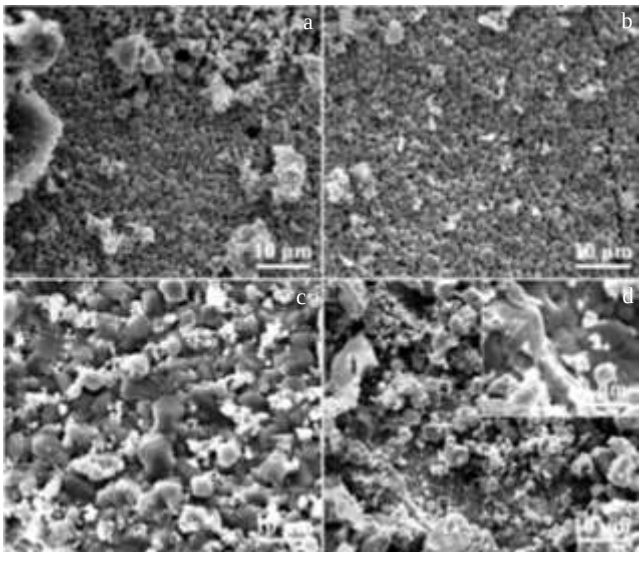

Fig.6 SEM images of ceramics derived from TS-5 (a), TS-10 (b), TS-25 (c) and TS-55 (d) hybrid precursors at 2273 K

that the conversion from precursor-to-ceramic is complete at around 1073 K, which is well consistent with the TG result. Further heating to 1673 K, the SiC_4 peak shifts from 780 cm^{-1} to 820 cm^{-1}, which is attributed to the formation of crystalline SiC. As a result, the TS-25 hybrid precursor converts to ceramic along with the conversion of organic to inorganic and amorphous to crystalline phase during the heat treatment.

The phase composition of ceramics derived from TS-25 at 873, 1073, 1273, 1473, 1673, 1873 and 2273 K was measured by XRD, as shown in Fig.4. It shows that TaC and SiC phases are not detected in the ceramic annealed at 873 K, just with appearance of crystal Ta. The initial formation of TaC, the characteristic peaks at 2θ=34.8° (111), 40.5° (200), 58.5° (220), 73.6° (222) and 87.5° (400), can be observed in pyrolyzed precursors at 1073 K, which indicates that the nano-Ta starts to convert to TaC at temperature around 1073 K. Further heating at 1673 K, the disappearance of the characteristic peaks of Ta indicates the nano-Ta is completely converted into TaC, meantime, weak peak appearing at 2θ=35.7° (111) is attributed to β-SiC. As the temperature increases to 2273 K, the characteristic peaks of TaC and β-SiC is sharper and sharper, which indicates the growth of crystal grains. As expected, TaC-SiC ceramics are successfully prepared via the pyrolysis of TS-25 hybrid precursor.

The effect of nano-Ta content in feed on the ceramics derived from TS-5, TS-10, TS-25 and TS-55 hybrid precursors at 1873 K was also investigated by XRD (Fig.5). As the nano-Ta content increases, the intensity of TaC peaks significantly increases.

Analyses on morphology and composition of ceramics annealed 2273 K derived from TS-5, TS-10, TS-25 and TS-55 were conducted by SEM-EDS. It is evident that the surface of TS-5 and TS-10 derived ceramics (Fig.6a and 6b) is porous, which may be caused by the severe evaporation of those volatile gases. As can be seen from Fig.6c and 6d, the ceramics are sintered without obvious phase separation, attributed to Ta increase, which plays an important role in the application as the ultrahigh temperature resistant materials. The components and contents of ceramics annealed at 2273 K derived from TS-55 were confirmed by EDS, and the results

Table 2 EDS analysis of TS-55 ceramics annealed at 2273 K in Fig.6d

Region	Ta content		Si content		C content	
	ω/%	at%	ω/%	at%	ω/%	at%
1	80.66	30.04	12.01	28.79	7.33	41.17
2	79.70	28.01	11.73	26.58	8.57	45.41
3	81.92	31.26	10.70	26.29	7.38	42.45
4	79.08	26.40	10.97	23.61	9.95	49.99
5	81.61	29.02	8.98	20.57	9.41	50.41
Average	80.59	28.95	10.88	25.17	8.53	45.89

are shown in Table 2. The ceramics are composed of tantalum, silicon and carbon and the composition of five regions is approximately the same, which indicates that the ceramics derived from TS hybrid precursor have uniform dispersion and could be stable without phase separation at high temperature. The average mass percentages of tantalum, silicon, carbon are 80.59%, 10.88%, 8.53%, respectively. According to the average atom percentages of these elements, the molar ratio of crystalline phase is calculated to be TaC/SiC = 1.15/1. It is worth mentioning that the molar ratio of the ceramic is approximately consistent with that of TS-55 hybrid precursor, indicating the composition of ceramics could be readily controlled by varying the Ta content in feed. Furthermore, the content of TaC is relatively high without excess carbon remaining in ceramic powders.

3 Conclusions

1) The hybrid precursors with uniform distribution are successfully prepared by blending nano-Ta and PCS via a ultrasonic and ball mill mixing method.

2) The ceramic yield of hybrid precursor increases with the increase of nano-Ta content, which indicates that the evolution of these volatile gases is inhibited via further cross-linking.

3) The precursor-to-ceramic transformation is completed at 1073 K; meantime, TaC crystal appears. Ta is completely converted into TaC at 1673 K. As the temperature or the nano-Ta content increases, the intensity of TaC peaks significantly increases.

4) The ceramics derived from TS hybrid precursors have uniform dispersion and stable phase composition.

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TaC-SiC 陶瓷的制备与表征

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摘 要：以纳米钽粉和聚碳硅烷为原料，采用超声和球磨混合方式按照钽粉分别为 5%、10%、25%、55%（质量分数）制备了不同陶瓷先驱体。通过 SEM、TG、IR、XRD、EDS 等表征先驱体的组成、结构以及裂解过程。结果表明：纳米钽粉均匀分散在聚碳硅烷中；先驱体的陶瓷产率随着 Ta 含量的增加而增加；1073 K 时先驱体基本无机化，Ta 开始转变为 TaC，1673 K 时，金属钽完全转化为 TaC；先驱体转化得到的陶瓷具有分布均匀、组成稳定等优点。

关键词：超高温；杂化先驱体；TaC-SiC；粉体

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