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Phase evolution of matrix of C/SiCN composite during creep testing at 1300 °C

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Tensile creep behavior of carbon fiber-reinforced SiCN matrix composite (C/SiCN) was investigated at 1300°C under vacuum and 45MPa for 30h. As-received and 1700°C-heat treated samples were prepared. Phase evolution and microstructure of C/SiCN was examined by virtue of X-ray diffraction, scanning electron microscope and high resolution transmission electron microscopy. It was found that crystallization happened in the as-received C/SiCN after 1300°C creep tested for 1h, though many researches indicate that the crystallization of amorphous SiCN occur above 1400°C heat treated. The matrix of as-received C/SiCN partly transformed from amorphous to β -SiC firstly and then α -SiC in the temperature range from 0h to 15h. The intensity of diffraction peaks had no significant change from 15h to 30h. The results revealed the applied stress promotes the occurrence of crystallization in as received C/SiCN. But the 1700°C-heat treated specimen showed little change of XRD patterns after creep testing.

1. Introduction :

Silicon carbonitride (SiCN) is an important material because of outstanding mechanical and thermal-mechanical properties at high temperatures. During the past decades, much effort has been focused on the synthesis and stability of SiCN [1 - 5]. Thermal stability and crystallization behavior of SiCN has been studied in many literatures [6 - 11]. To overcome the intrinsic brittleness and improve the toughness of monolithic SiCN ceramic, some kinds of long fiber reinforced SiCN composites have been developed. Also mechanical properties of long fiber reinforced SiCN composites have been studied [12, 13]. As an important mechanical property of high temperature materials, creep property must be studied.

Many researches have been made on the creep behaviors and mechanism of ceramic matrix composite (CMC) [14]. Boitier reported that the potential creep of the carbon fibers could be followed according to the dimensional evolution of basic structural unites (BSUs) and local molecular orientation (LMOs), and the creep mechanism for C_F-SiC was damage creep [15, 16]. However, most of the creep researches on SiCN are compression or bending creep [17 - 19], almost no tensile creep has been conducted on long fiber reinforced SiCN composites and less attention has been given to SiCN phase evolution during tensile creep.

It is believed that the applied stress could promote the phase evolution of amorphous SiCN, so the crystallization behavior of SiCN ceramic under applied load is an interesting topic. In the present study, tensile creep has been conducted on carbon fiber-reinforced SiCN matrix

composite (C/SiCN) at 1300°C under vacuum condition. Much attention has been given to phase evolution C/SiCN in this process.

2. Experimental :

2.1 Materials and sample preparation :

The C/SiCN composite was prepared by rapid electro-thermal pyrolysis chemical vapor deposition (CVD), the detailed processing has been described in lately patent [20]. The reinforcements used here were 2.5D fabric preform (4.0 mm in thickness) of ex-PAN carbon fiber (T-300 1K, Nippon Toray Corporation), whose schematic was shown in Figure (1). In order to maximize the strength, toughness and oxidation resistance of composite, before preparing composite, ~ 300 nm glass-like carbon (GC) was deposited on the fiber by polymer infiltration and pyrolysis (PIP) using phenolic resin as precursor. The polymer precursor utilized to prepare SiCN ceramic matrix was commercially available hexamethyldisilazane ((CH₃)₃SiNHSi(CH₃)₃, boiling point : 126°C; Purity : ≥99.0%).

Two kinds of samples were prepared with C/SiCN, one was heat treated at 1700°C for 2h in vacuum and the other was as received condition.

2.2 Apparatus and Procedures :

Tensile creep test was carried out at 1300 °C under vacuum, and the creep stress was 45 MPa. The experiment was stopped for phase observation after creep tested for 1 h, 5 h, 15 h, and 30 h. The initial gauge length and rectangular cross-section were 50 mm and 3.4×3.0 mm, respectively.

X-ray fluorescence (XRF, BRUKER AXS) was used for chemical composition of the as received material. X-ray diffraction (XRD) patterns of the samples were obtained by an X-Pert Pro X-ray diffractometer (made by Panalytical B. V, Holland), with $\text{CuK}\alpha$ radiation.

The microstructure of the C/SiCN before and after creep was observed by scanning electron microscope (SEM) (S-4700, Hitachi, Japan). The morphology and selected-area electron diffraction (SAED) patterns are examined by a high resolution transmission electron microscopy (HRTEM) (Model JEM-2100F, Japan) at the accelerating voltage of 200 kV.

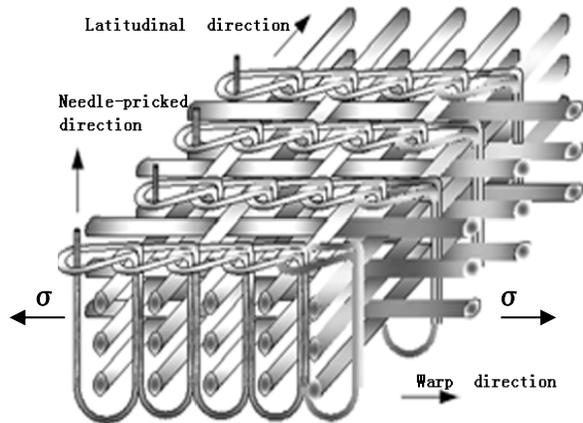


Figure (1) : Schematic of carbon fiber perform.

3. Results and Discussion

As showed in Table (1), the atomic composition of matrix of the as received C/SiCN is $\text{Si}_{39.5}\text{C}_{40.6}\text{N}_{14.6}$. XRD analysis in Figure (2) reveals that matrix of the as received C/SiCN is fully amorphous. And SEM observation in Figure (3) shows some pre-existing cracks and pores of several micrometer scales exist on the cross section of the as received C/SiCN.

Table (1) : XRF result of the as-received SiCN matrix

	C	N	O	Al	Si	K	Ca
wt%	25.51	10.69	4.43	0.43	55.51	0.18	0.24
at%	40.6	14.6	5.3	-	39.5	-	-

The HRTEM images of the as-received and the 1700 °C-heat treated C/SiCN are shown in Figure (4). In Figure (4a), the bonding morphology of SiCN matrix, GC interface and C fiber is clearly distinguished, and the thickness of interface is about 300 nm. The corresponding selected area electron diffraction (SAED) of SiCN matrix also reveals its amorphous nature. After heat treated at 1700 °C for 2 h in vacuum, some crystals have appeared in the matrix (Figure 4b), and these crystals are mainly β -SiC after indexing.

The HRTEM bright field image showing the microstructure of the 1700 °C-heat treated SiCN ceramic was shown in Figure (5). It displays the nanostructure of

SiCN ceramics consists of dispersed nanosized SiC crystallites embedded in the amorphous SiCN matrix. The size of the crystal grain is about 60-80 nm. And several crystallites stack on each other and look like cloud. From the high magnification images of the crystallite, it could be easily found that the atom regularly arranged and the crystallites grow perfect. The high magnification image of the area between crystallites shows that the SiCN is not absolutely amorphous, some turbostratic carbon appears.

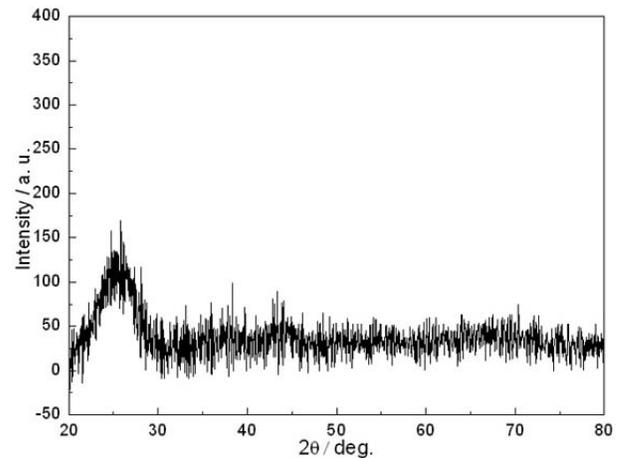


Figure (2) : XRD patterns of as-received C/SiCN.

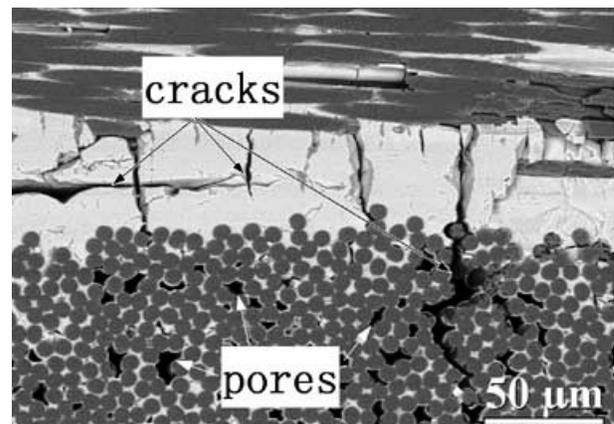


Figure (3) : SEM images of cross-section of C/SiCN.

It could be easily found that both of the C/SiCN samples heat treated and as received only exhibit two stages of creep behavior in Figure (6). Creep curves for two kinds of C/SiCN samples are similar. The total strain is very small, in micro-scale. But the maximum strain of as-received sample is a little greater than that of the heat treated sample and the former needs less time to get into the steady-state creep. This phenomenon may be related to the matrix phase evolution during the creep test because the phase evolution of SiCN matrix would lead to volume change and discharge some kinds of gas such as H_2 and N_2 . If gas discharged from the matrix, some pores would be left in the matrix. So the matrix would deform much more easily. As a result, it is needed to further study the phase evolution of C/SiCN during creep.

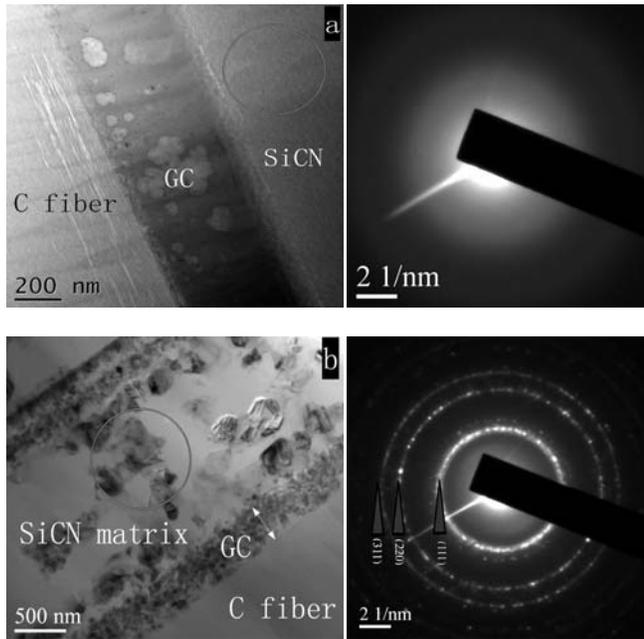


Figure (4) : HRTEM images showing the microstructure of C/SiCN (a)as-received; (b) the 1700°C-heat treated.

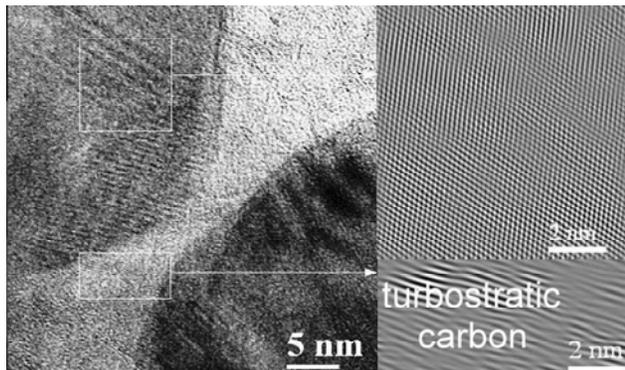
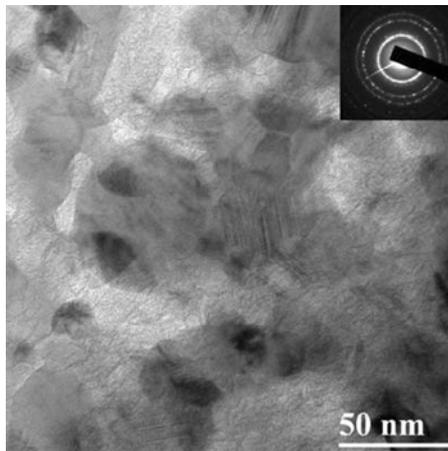


Figure (5) : Bright field images of the 1700 °C-heat treated SiCN ceramic.

XRD patterns of C/SiCN after creep tested for different time are shown in Figure (7). Figure (7a) shows the phase evolution of as received C/SiCN. From Figure

(7a) 0 h XRD pattern, it can be found that three faint diffraction peaks appear at $2\theta = 35.6^\circ$, 60° and 72° . Obviously, they are the diffraction peaks of (111), (220) and (311) crystal plane of β -SiC. This indicates that the matrix of the as received C/SiCN begins crystallization only after creep tested for 1h. These three diffraction peaks become sharper in the 5 h XRD pattern and get sharpest in the 15 h XRD pattern. In the 15 h XRD pattern, two more diffraction peaks appear at $2\theta = 34.1^\circ$ and 38.2° , it means some β -SiC transforms to α -SiC. The intensity of diffraction peaks almost has no change from 15 h to 30 h. This suggests that there is no significant phase transformation during 15 h to 30 h. The crystallization behavior of as received is different from that reported in some other literatures. G. Gregori reported that bulk SiCN remained predominantly amorphous after heat treatment at 1400°C [21]. Günter Turn concluded that no crystalline phases had been found in monolithic SiCN after compression creep at 1400°C and lower temperatures [22]. And Liew's study indicated that amorphous SiCN would be stable below 1500°C [23]. Besides the compositions of SiCN in present work is different from that studied in above literatures, the tension creep stress may lead to the active energy of phase evolution decrease, so at 1300°C during initial creep stage, the amorphous SiCN will transfer gradually to crystal phases. SEM image of fracture surface of matrix of C/SiCN in Figure (8) shows some micro-scale pores which may indicate that some gases were discharged during creep testing. As known to all, most of precursor derived SiCN ceramic contains nitrogen and hydrogen atoms. In temperature range between 800°C and 1200°C , the hydrogen is eliminated [24]. This point can be confirmed by the phenomenon that vacuum degree of the creep machine declined at heating temperature above 800°C observed during the experiment. And further heat treatment causes the decrease of nitrogen content in the ceramic material because of its release as N_2 [24].

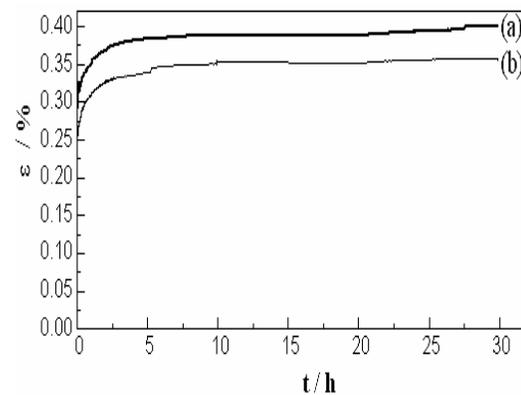


Figure (6) : The creep curves C/SiCN (a)as-received; (b) the 1700°C-heat treated.

Figure (7b) shows the phase evolution of the heat treated C/SiCN. The intensity and amount of diffraction peaks in Figure (7b) are almost the same from 0 h to 30 h, which indicates that matrix of the heat treated samples is relatively stable. As showed in Figure (5), some turbostratic

carbon in the amorphous SiCN may be the reason. This configuration, in turn, acts as a diffusion barrier, similar to B(C)N formation in Si-B-C-N ceramics [25], restricting local crystallization. The only change is that 2θ degree of the three most intensive peaks decline, especially for the most intensive peak representing β -SiC (111) crystal plane, it shows that crystal plane spacing along to (111) increases according to Bragg's law.

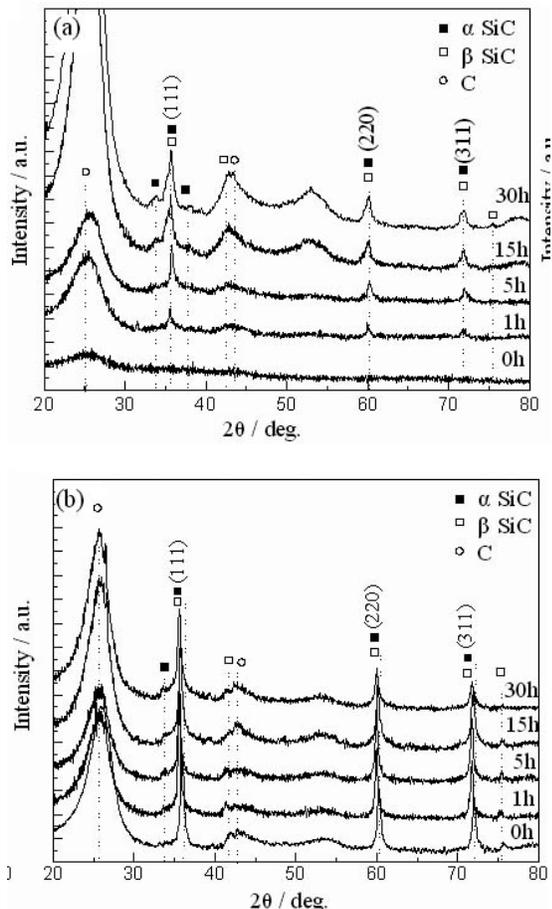


Figure (7) : XRD patterns of C/SiCN after creep tested for different time (a) the as-received; (b) the 1700°C-heat treated.

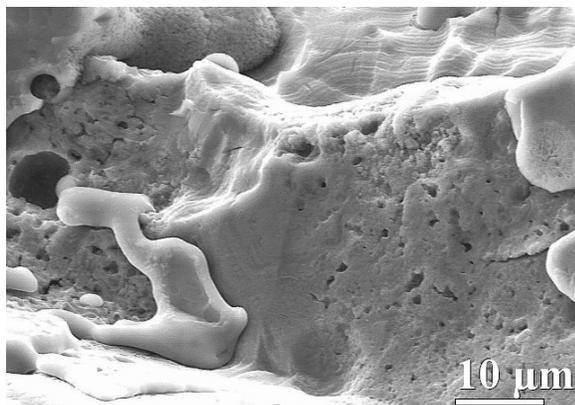


Figure (8) : SEM images of fracture surface of C/SiCN.

4. Conclusions :

Matrix of C/SiCN as received is fully amorphous. Tensile creep behavior of C/SiCN at 1300 °C exhibits two stages. Crystallization happened in the as-received C/SiCN after creep tested for 1 h. The matrix of as-received SiCN partly transformed from amorphous to β -SiC firstly and then α -SiC in the temperature range from 0 h to 15 h. The intensity of diffraction peaks had no significant change from 15 h to 30 h. The results revealed the applied stress promotes the occurrence of crystallization of matrix of as received C/SiCN. But the 1700 °C-heat treated specimen showed little change of XRD patterns besides the decline of 2θ degree of the three most intensive peaks after creep testing.

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