

# CREEP RUPTURE OF 3-D WOVEN Si-Ti-C-O FIBER/SiC-BASED MATRIX COMPOSITE WITH GLASS SEALANT

Toshio Ogasawara<sup>1</sup>, Takashi Ishikawa<sup>1</sup>, Naoto Suzuki<sup>1</sup>, Ian J. Davies<sup>2</sup>,  
Michiyuki Suzuki<sup>3</sup>, Jun Gotoh<sup>4</sup> and Tetsuro Hirokawa<sup>5</sup>

<sup>1</sup>*National Aerospace Laboratory (NAL), 6-13-1 Ohsawa, Mitaka, Tokyo, 181-0015, Japan*

<sup>2</sup>*Kyoto Institute of Technology, Matsugasaki, Sankyo-Ku, Kyoto, 606-8585, Japan*

<sup>3</sup>*Ube Industries Ltd., Ube, Yamaguchi, 755-8633, Japan*

<sup>4</sup>*Kawasaki Heavy Industries Ltd., Kagamigahara, Gifu, 405-8710, Japan*

<sup>5</sup>*Shikibo Ltd., Yokaichi, Shiga, 517-8577, Japan*

**SUMMARY:** The present work investigates the tensile creep behavior (deformation and rupture) at 1100-1300 °C in air of a 3-D woven Si-Ti-C-O (Tyranno™) fiber/SiC-based matrix composite with and without glass sealant. The composite contained Si-Ti-C-O fibers with an additional surface modification in order to improve interface properties. Although a significant decrease in tensile strength was observed in the unsealed composite beyond 1000°C in air (and attributed to oxidation of the fiber/matrix interface), the composite with glass sealant possessed excellent mechanical properties for short-term (<1hr.) exposure in air. In this study, tensile creep testing was conducted at 1100-1300 °C in air and the effect of glass sealant on medium- and long-term strength was investigated. In addition, chemical stability of the glass sealant was evaluated by X-ray diffraction analysis. The creep rupture behavior of the composite with glass sealant under long-term exposure is suggested to depend on several factors including decomposition, evaporation, and crystallization of the glass sealant material, in addition to the applied stress.

**KEYWORDS:** ceramic matrix composite, textile, creep, silicon carbide, interface, crystallization, X-ray diffraction

## INTRODUCTION

Monolithic ceramics typically do not possess the toughness required for aerospace applications. For this reason, significant effort has been devoted to the development of ceramic matrix composites (CMCs) with continuous ceramic fiber reinforcement such as SCS-6™, Nicalon™, and Tyranno™. The National Aerospace Laboratory of Japan, Ube Industries Ltd., Shikibo Ltd., and Kawasaki Heavy Industries Ltd. have conducted a joint program in order to develop and evaluate a ceramic matrix composite. The composite contains Tyranno™ (Si-Ti-C-O) fibers with an additional surface modification in order to improve interface properties. Thus, the fiber/matrix interface is controlled by the heat treatment of the fiber in a carbon monoxide (CO) atmosphere with a SiO<sub>x</sub>-rich layer surrounding an inner carbon-rich layer being formed at the fiber surface. Using such technology, the composite exhibits excellent tensile strength (~400 MPa) at room temperature [1]. However, a significant decrease in tensile strength was observed in the composite beyond 1000 °C in air and this was attributed to

oxidation of the fiber/matrix interface and subsequent increase in the fiber debonding shear strength. On the other hand, composite with an additional glass sealant possessed excellent mechanical properties for short-term (<1hr.) exposure up to 1300 °C in air and in vacuum [2]. In general, the carbon-rich interface layer in SiC/SiC-based composites shows low oxidation resistance at elevated temperature in air and hence the glass sealant may act as an oxygen diffusion barrier within the composite. A similar phenomenon has been observed in a glass-including matrix Nicalon/SiC-based composite developed by DuPont Lanxide Composites (Wilmington, DE, USA). This composite, termed “enhanced SiC/SiC composite”, exhibits excellent strength at 1300 °C in air [3].

The present work will investigate the tensile creep behavior (deformation and rupture) of the composite and the effect of glass sealant on tensile strength at 1100-1300 °C in air. Chemical stability of the composite with glass sealant at elevated temperature was also evaluated.

## EXPERIMENTAL PROCEDURE

The composite under investigation contained Tyranno™ Lox-M fibers woven into an orthogonal 3-D configuration with fiber volume fractions of 0.19, 0.19, and 0.02 in the x, y, and z directions, respectively. The resulting composite preform plate (240 x 120 x 6 mm) was treated at elevated temperature in a CO atmosphere, resulting in formation of a 10 nm SiO<sub>x</sub>-rich layer surrounding an inner 40 nm carbon-rich layer at the fiber surface [1].

Polytitanocarbosilane was used as the matrix precursor with repeated impregnation and pyrolysis cycles until satisfactory densification was achieved. Tensile specimens were machined from the composite plates such that the loading direction was parallel to the y axis. An optical micrograph illustrating the composite fiber architecture has been presented in Fig. 1 with each fiber bundle containing 1600 fibers. Following machining, tensile specimens were impregnated with a proprietary SiO<sub>2</sub>-Na<sub>2</sub>O-based water glass. The impregnation process was repeated several times with the aim of improving resistance to oxidation.

Monotonic tensile and creep testing was conducted on a servo-hydraulic testing system (Model 8501, Instron, USA) at room temperature, 1100 °C, 1200 °C, and 1300 °C in air. The high temperature furnace and contact-type extensometer used for these experiments have been shown in Fig. 2. The specimen gage length was 12.5 mm whilst specimens were held for 3 minutes at the test temperature prior to monotonic tensile or creep testing. Monotonic tensile tests were conducted under a constant displacement rate of 0.5 mm/min whilst the time to reach the required stress for creep testing was 3 minutes following holding.

Specimen fracture surfaces were observed using a scanning electron microscope (SEM)

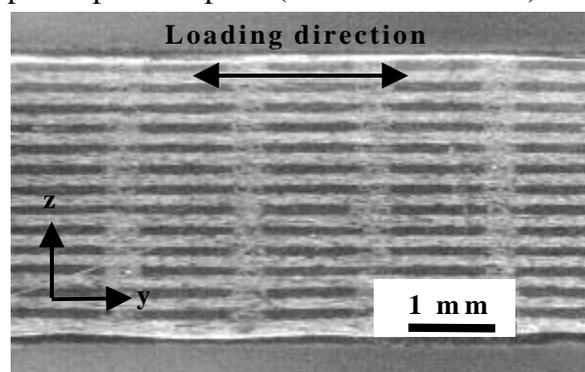


Fig.1: Optical micrograph of SiC/SiC-based composites illustrating the 3-D woven fiber configuration (yz plane)

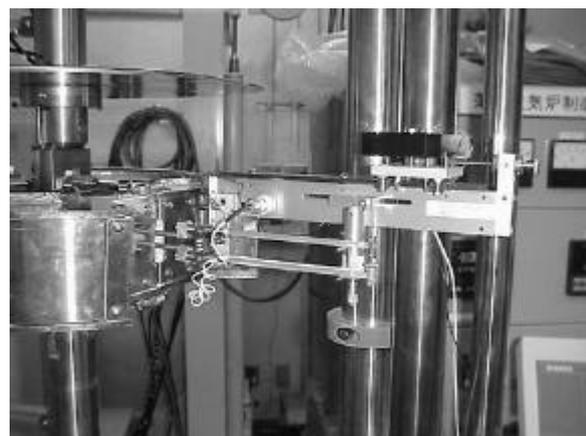


Fig.2: Extensometer and high temperature furnace used for monotonic loading and creep testing.

(Model JSM-6300F, JEOL, Japan). X-ray diffraction (XRD) analysis was conducted using a Cu-K $\alpha$  source (Model RINT2000, Rigaku, Japan) in order to investigate crystallization of the glass phase during creep testing.

## RESULTS AND DISCUSSION

### Monotonic tensile behavior

The ultimate tensile strength,  $S_{UTS}$ , of specimens as a function of test condition has been presented in Fig. 3.  $S_{UTS}$  for unsealed specimens was equivalent at room temperature and 1200 °C in vacuum but decreased rapidly for unsealed specimens tested in air at 1100-1200 °C. The latter trend was attributed to oxidation of the fiber/matrix interface that resulted in a transformation from “pseudo-ductile” to brittle fracture behavior. However,  $S_{UTS}$  for specimens tested in air at 1000-1300 °C was significantly improved by the addition of glass sealant, indicating the sealant to protect against oxygen ingress for at least the time scale investigated (on the order of several minutes).

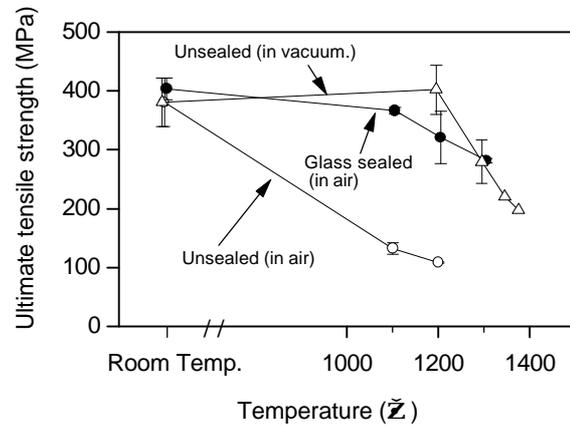


Fig.3: Ultimate tensile strength of the composites tested in vacuum and air at elevated temperature

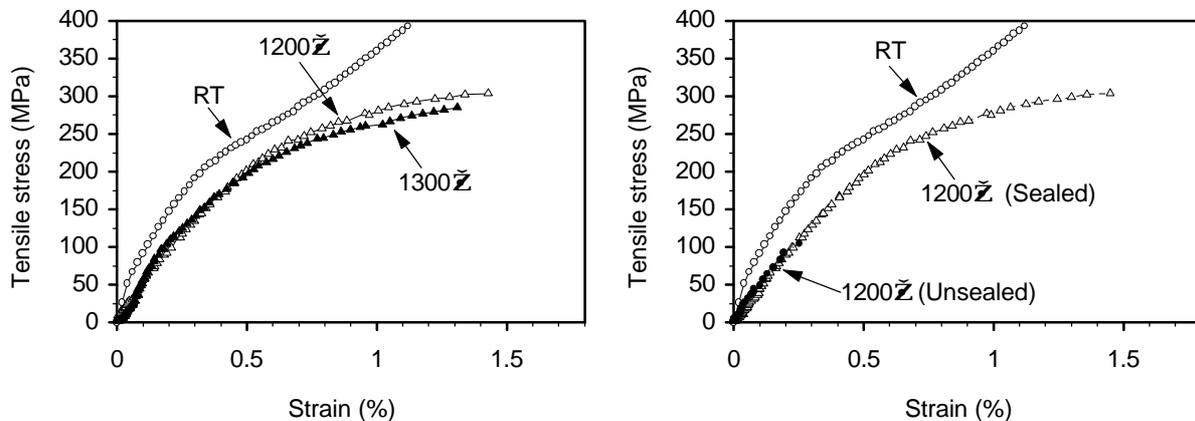


Fig.4: Typical monotonic tensile stress versus strain for sealed and unsealed composite at 1200°C /air under a constant displacement rate 0.5 mm/min.

Composite stress-strain curves exhibited an initial linear response followed by non-linear behavior (shown in Fig. 4) for unsealed specimens and sealed specimens in air. However, unsealed specimens showed only the initial linear region prior to failure, suggesting the fibers to have played almost no toughening role in this case and attributed to oxidation of the fiber/matrix interface. The glass sealant material was found to have no significant influence on the composite stiffness, in contrast to the case of “enhanced SiC/SiC composite” [3]. The proportional stress limit,  $\sigma_{PL}$ , was approximately 150-170 MPa at elevated temperature. Although matrix cracks in the 0° bundles (y axis) were thought to occur only above  $\sigma_{PL}$ , transverse cracks in the 90° bundles (x and z axis) may well have appeared prior to  $\sigma_{PL}$ . As mentioned above, the composite fiber/matrix interface shear strength,  $\tau$ , was controlled by a

thin (40 nm) carbon layer formed by heat treatment of the fiber in a CO atmosphere. Therefore, oxidation of the carbon interface in the unsealed composite would be expected to occur rapidly at elevated temperature in air. The effect of test condition on  $\tau$  for unsealed and sealed composite has been presented in detail elsewhere [2,4].

### Creep deformation and rupture behavior

Creep rupture data for sealed composite tested at 1100-1300 °C in air has been summarized in Fig. 5. Although the data is seen to have considerable scatter, it would appear that a change in the creep strength degradation behavior occurs in the long-term region at approximately  $1-2 \times 10^6$  sec (200~300 hr.) for the 1100 °C case and  $3-4 \times 10^5$  sec (~100 hr.) at 1200 °C. However, this change in creep behavior was not observed at 1300 °C.

The relationship between creep deformation and time at 1200 °C and 1300 °C has been shown in Fig. 6. A steady state creep region, in which the creep rate was constant, can be observed in both cases. The relationship between applied stress and steady state creep rate has been presented in Fig. 7. In the low stress range, the steady state creep rate was found to be insensitive to the applied stress and the stress exponent,  $n$  [5], in this region was 1-2 at both 1100 and 1200 °C whilst the value of  $n$  in the higher stress region ( $>150-170$  MPa) was 7-9, again for both cases. Similar results have been reported for SiC-fiber (SCS6)/Si<sub>3</sub>N<sub>4</sub> 0° composite [6] and SiC-fiber (Nicalon)/MLAS 0-90° ply

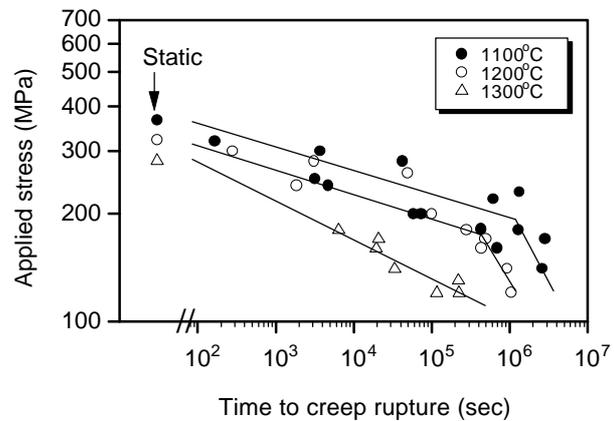


Fig.5: Creep rupture data for sealed composite at 1100°C-1300°C in air

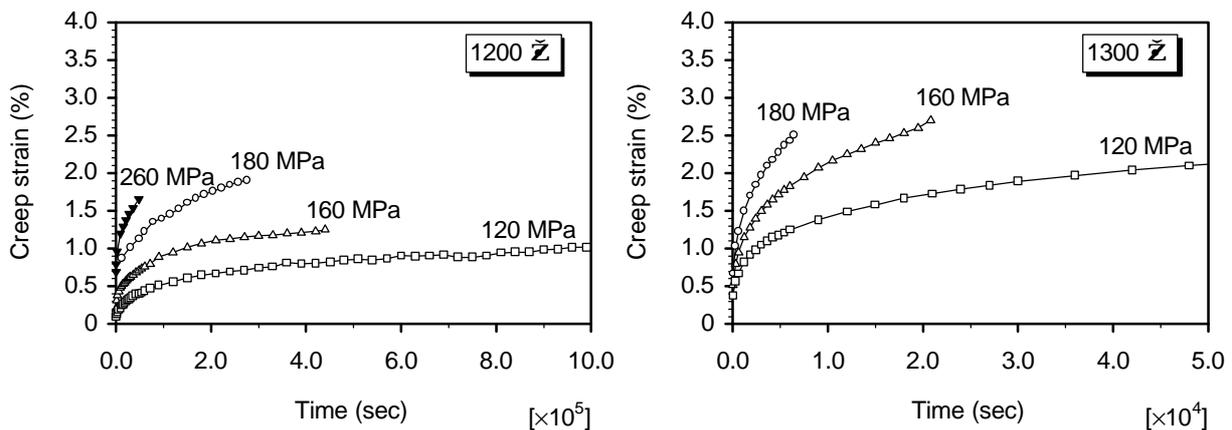


Fig.6: Tensile creep strain versus time of the glass sealed composite at 1200°C and 1300°C in air composite [7].

The transition stress where the stress exponent changes is believed to correspond to the proportional stress limit (150-170 MPa) in the composite stress-strain curve at elevated temperature (Fig. 4). The stress exponent in the high stress region is also similar to that of “enhanced SiC/SiC composite” reported by Zhu et al. [3]. The stress exponent in the low stress region was similar to that for Si-C-O fibers used in previous work [5,8]. These experimental results indicate that matrix cracks in the 0° bundles have a significant influence on the composite creep deformation.

Transverse and matrix cracks that arise during loading at room temperature may be arrested due to the R-curve behavior, i.e., fiber bridging mechanism. However, at high temperature, time-dependent matrix crack growth may take place due to a combination of stress corrosion cracking and creep crack growth of the matrix. The crack opening displacement (COD) contribution from matrix cracks would also be expected to increase due to fiber creep within the matrix cracks. Such slow crack growth and fiber creep increases the specimen compliance and also the steady state creep rate.

SEM micrographs of specimen fracture surfaces following creep testing at 1200 °C have been shown in Fig. 8. It has previously been confirmed by several of the authors that  $S_{UTS}$  for this composite is closely predicted by the equation of Curtin [9]:

$$S_{UTS} = V_f S_0^* \left( \frac{2}{m+2} \right)^{\frac{1}{m+1}} \left( \frac{m+1}{m+2} \right) \quad (1)$$

Where  $S_0^*$  and  $m$  are the *in situ* fiber strength Weibull parameters obtained from fractography studies, and  $V_f$  is the fiber volume fraction in the direction of loading.

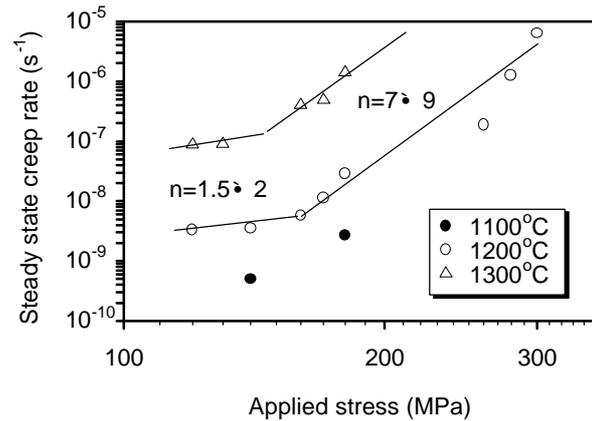


Fig.7: Steady state creep rate in air versus applied stress for sealed composite

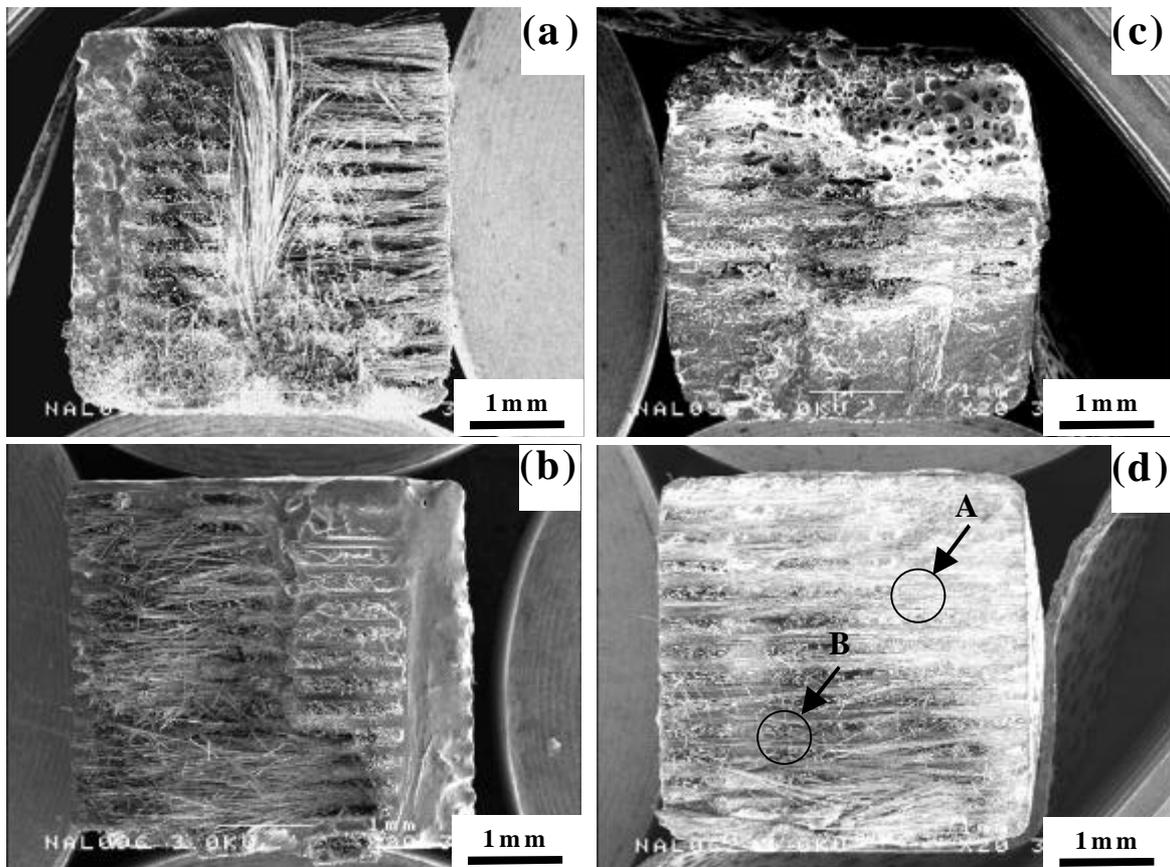


Fig.8: Scanning electron micrographs illustrating fracture surfaces of 3-D woven SiC / SiC based composite after monotonic tensile and creep testing at 1200°C /air:(a) monotonic loading rupture ( $UTS$ , 289 MPa), (b) creep rupture (200 MPa, 2080 sec), (c) creep rupture (200 MPa,  $4.4 \times 10^5$  sec), (d) creep rupture (120 MPa,  $1.05 \times 10^6$  sec).

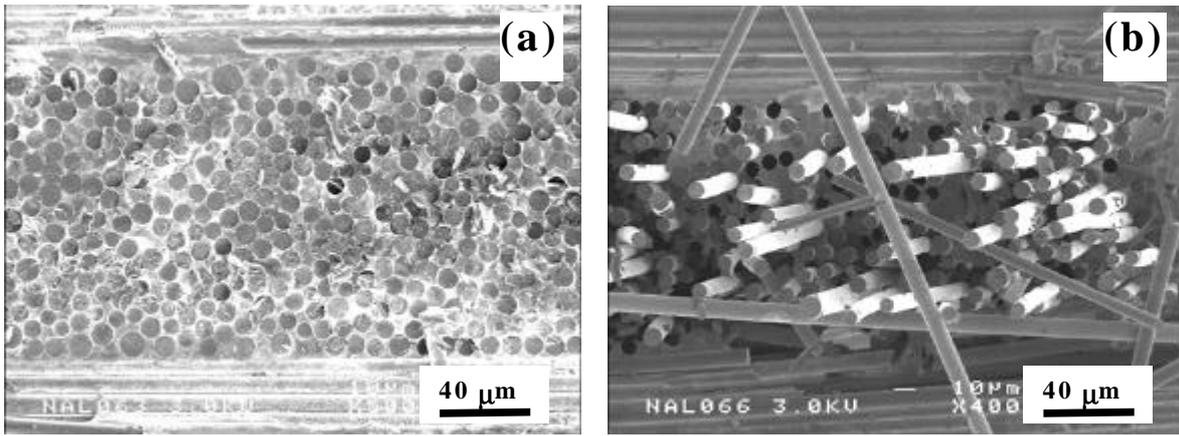


Fig.9: Scanning electron micrographs illustrating fracture surfaces of 3-D woven SiC/ SiC based composite after creep testing for  $1.05 \times 10^6$  sec at  $1200^\circ\text{C}$  /air: (a) and (b) are correlated to regions indicated by the arrows shown in Fig.8(d).

Should all the fibers not be able to contribute to  $S_{UTS}$  (for example, due to degradation of the fiber/matrix interface) then  $V_f$  should be replaced by the effective fiber volume fraction,  $V_{eff}$ .

The unsealed composite  $S_{UTS}$  at elevated temperature in air is known to be significantly influenced by fiber strength degradation and increased interfacial shear stress [2]. In addition, increased interfacial shear stress results in the effective fiber fraction being decreased as the number of fibers at which crack deflection takes place is significantly reduced. In effect, the number of fibers that contribute to the composite  $S_{UTS}$  decreases with a degradation of fiber/matrix interface properties (i.e., increase in  $\tau$ ).

Fig. 9 presents SEM micrographs taken from two regions in Fig. 8(d) marked “A” and “B”. The first micrograph (Fig. 9(a)) shows a fiber bundle that exhibits significant fiber pullout and hence can be thought of as “effective fibers” that contribute to the composite  $S_{UTS}$ . However, Fig. 9(b) indicates region “B” from Fig. 8(d) to have a flat fracture surface with negligible fiber pullout. In this case, oxidation of the fiber/matrix interface has increased  $\tau$  to such an extent that crack deflection did not occur at the fiber/matrix interface – these fibers were thought to have negligible contribution to the composite  $S_{UTS}$ .

This phenomenon was investigated further by estimating the size of “oxidized” and “non-oxidized” (i.e., unaffected by oxygen ingress) regions from fracture surface analysis. The resulting data has been presented in Fig. 10 in the form of oxidized region volume fraction,  $OR_{VF}$ , as a function of creep stress,  $C_s$ . Considering the difficulty in deciding the boundary position between oxidized and non-oxidized regions, a fairly good correlation can be observed in Fig. 10 with  $OR_{VF}$  increasing with decreasing  $C_s$ . It is clear from this that final composite failure occurs when the remaining “non-oxidized” fibers are not able to sustain the applied creep stress. Linear curve fitting showed  $C_s$  to be  $317 (\pm 23)$  MPa at  $OR_{VF}=0$  which, again considering the simplistic nature of the calculation, is only  $\sim 20\%$  lower than  $S_{UTS}$  at room temperature. Therefore, it may be concluded that those fibers and their interfaces in the unoxidized region should have almost no oxidation damage.

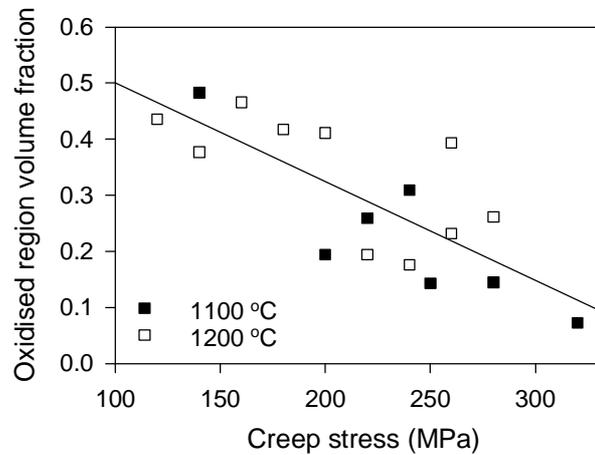


Fig. 10: Volume fraction of oxidised region estimated from fracture surface vs. creep stress in air for 3-D woven SiC/SiC-based composite.

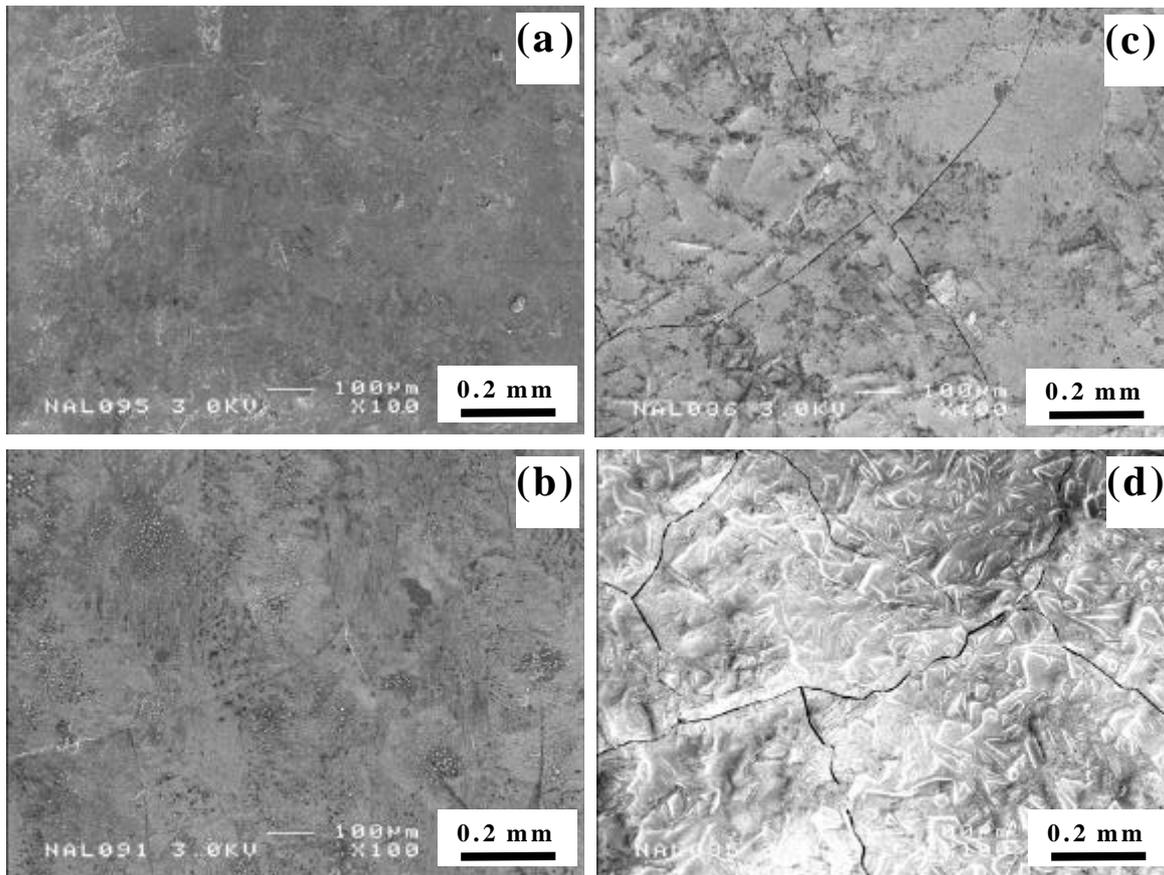


Fig.11: Scanning electron micrographs illustrating the sealed composite surface for 3-D woven Si-Ti-C-O/ Si-C based composite: (a) prior to exposure, and following creep testing at 1200°C /air: (b)  $2.08 \times 10^3$  sec, (c)  $4.4 \times 10^5$  sec, (d)  $1.05 \times 10^6$  sec.

SEM micrographs of specimen surfaces prior to and following creep testing at 1200 °C have been shown in Fig. 11. It should be noted that these micrographs were taken following cooling and hence may not accurately represent the actual glass sealant surface morphology at elevated temperature. The glass sealant in Fig. 11 is smooth prior to creep testing (Fig.11(a)) but becomes progressively rougher with increasing creep time. Figs.11(c) and 11(d) show strong evidence of the presence of crystal structures within the glass sealant and this was confirmed by XRD with data being presented in Fig. 12.

From Fig.12, it is clear that the crystal structure of both fiber and matrix (“unsealed (new)”) is polytypic silicon carbide with a very small crystalline size deduced from the relatively broad peak. The sealed specimen prior to creep testing (“sealed (new)”) exhibited a small amount of SiO<sub>2</sub> (tridymite) that derived from the glass sealant. The tridymite diffraction peak intensity increased with exposure time and increased rapidly after  $3-4 \times 10^5$  sec

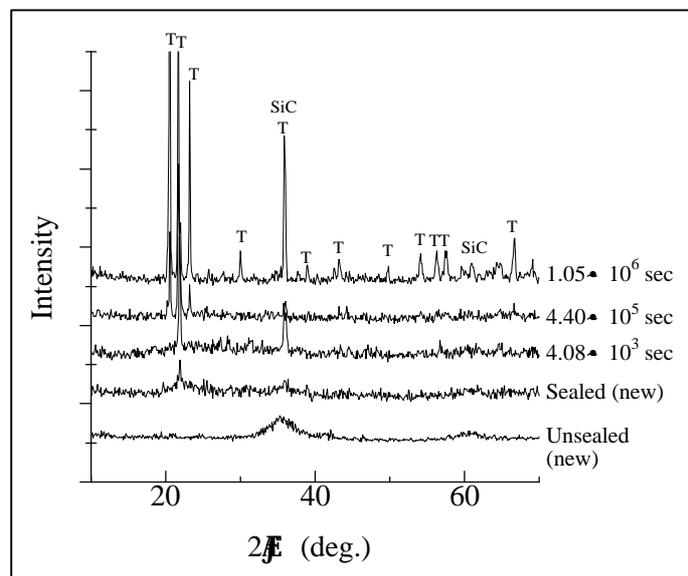


Fig.12: X-ray diffraction patterns from the composite surface before and after creep testing at 1200°C in air

(~100 hr.) of exposure. This exposure time corresponds to the time at which the creep strength decreased significantly (Fig. 5). Therefore, it may be the case that the effectiveness of the glass sealant decreases with increasing crystallinity due to such factors as increased viscosity and volume contraction.

SEM observation of fracture surfaces following creep testing showed initial ingress of oxygen into the specimen to occur mainly at the specimen corner (13 out of 17 specimens examined). In three of the remaining specimens, oxygen ingress initiated halfway along the specimen edge at the point where the z direction fiber bundle was closest to the specimen surface. The remaining specimen failed due to a large defect within the composite body. Figure 13(a) is a SEM micrograph of a specimen that failed after  $2.63 \times 10^6$  sec exposure to 1100 °C at 140 MPa. Fig. 13(b) is a schematic representation of the fracture surface showing the expected oxygen path, fiber bundle positions, and boundary between the “oxidized” and “non-oxidized” regions.

One explanation for failure initiation is that the oxidation region may correspond to matrix cracks, i.e., transverse cracks in 90° fiber bundles and matrix cracks in 0° bundles. Glass sealant with a suitably low viscosity to cover the specimen surface and matrix cracks will be effective as an oxygen diffusion barrier. The glass sealant would cover the specimen surface uniformly and restrict oxygen diffusion into the matrix cracks as shown in Fig. 14. At the crack surface and tip, glass sealant impregnated within the composite may also be effective as an oxygen diffusion barrier. The size of the oxidation region would be expected to increase with continued loading due to time dependent crack growth factors such as stress corrosion cracking and creep crack growth. Increased viscosity of the glass sealant under long-term exposure, due to the crystallization, would make it difficult for the glass sealant to uniformly cover the composite and crack surface. At this point the glass sealant’s function as an oxygen barrier would be degraded. Thus, the creep rupture behavior of the glass sealed composite for long-term exposure would appear to depend not only on the applied stress but also on crystallization of the glass sealant material.

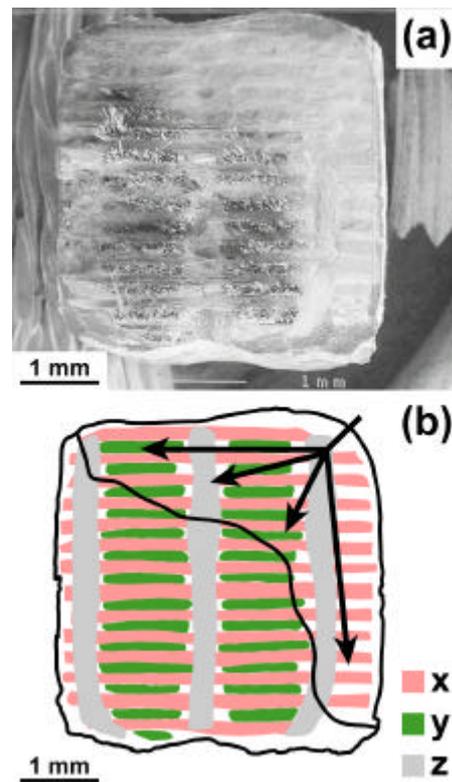


Fig. 13: Fracture surface of a 3-D woven SiC/SiC-based composite after creep testing in air (1100 °C/140 MPa/ $2.63 \times 10^6$  sec): (a) SEM micrograph, and (b) schematic representation of fracture surface showing fibre bundle positions, oxygen path within composite, and boundary between oxidized and non-oxidized regions.

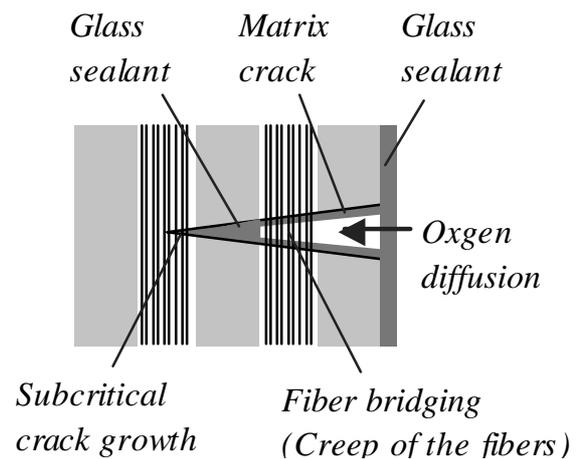


Fig.14: Schematic drawing of matrix crack and glass sealant during creep testing

Another possible explanation or contributory factor is that it may be easily shown that the glass evaporation rate will increase with decreasing radius of curvature for the specimen surface. Therefore, the maximum glass evaporation rate for these specimens would be at their maximum at the corner regions. Initial differences in glass sealant thickness between the corner and planar regions of the specimen surface also cannot be ruled out.

## CONCLUSIONS

The tensile creep behavior (deformation and rupture) in air at 1100-1300 °C of a 3-D woven Si-Ti-C-O (Tyranno™) fiber/SiC-based matrix composite with glass sealant was investigated. The following conclusions were made:

- (1) Although the creep rupture data possessed considerable scatter, the creep strength degradation behavior appeared to change in the long-term region at approximately  $1-2 \times 10^6$  sec (200~300 hr.) for specimens tested at 1100 °C, and  $3-4 \times 10^5$  sec (~100 hr.) for those at 1200 °C.
- (2) The stress exponent,  $n$ , was 7-9 in the high stress region (>150-170 MPa) and 1-2 in the low stress region at both 1100 °C and 1200 °C. The stress exponent in the low stress region was similar (1-2) to that of Si-C-O fibers found in the literature. The transition stress where the stress exponent changed was found to correspond to the proportional limit stress under monotonic tensile loading.
- (3) According to XRD analysis of specimen surfaces following creep testing at 1200 °C, crystallization of the glass phase increased rapidly after an exposure time of  $3-4 \times 10^5$  sec and this corresponded to the time at which the creep strength significantly decreased.
- (4) The creep rupture behavior of the composite with glass sealant under long-term exposure is suggested to depend on a combination of factors such as crystallization of the glass sealant material, specimen geometry, and variations in the glass evaporation rate, in addition to the applied stress

## REFERENCES

- [1] Ishikawa, T., Bansaku, K., Watanabe, N., Nomura, Y., Shibuya, M. and Hirokawa, T., "Experimental Stress/Strain Behavior of SiC-Matrix Composites Reinforced with Si-Ti-C-O Fibers and Estimation of Matrix Elastic Modulus", *Comp. Sci. Tech.*, 58, 1998, pp.51-63
- [2] Davies, I. J., Ishikawa, T., Shibuya, M., Hirokawa, T., and Gotoh, J., "Fibre and interfacial properties measured *in situ* for a 3-D woven SiC/SiC-based composite with glass sealant", *Composites Part A*, 30(4) pp. 587-591 (1999)
- [3] Zhu, S., Mizuno, M., Nagano, Y., Cao, J., Kagasa, Y. and Kaya, H., "Creep and Fatigue Behavior in an Enhanced SiC/SiC Composite at High Temperature", *J. Am. Ceram. Soc.*, 81[9], 1998, pp. 2269-77
- [4] Davies, I. J., Ishikawa, T., Shibuya, M., and Hirokawa, T., "Fibre strength parameters measured *in situ* for ceramic matrix composites tested at elevated temperature in vacuum and air", *Comp. Sci. Technol.*, *in press*
- [5] DiCarlo, J. A., "Creep Limitations of Current Polycrystalline Ceramic Fibers", *Comp. Sci. Tech.*, 51, 1994, pp. 213-222
- [6] Holmes, J. W., "Creep Behavior of Continuous Fiber-Reinforced Ceramics", *High Temperature Mechanical Behavior of Ceramic Composites*, Ed. By Nair, S. V. and Jakus, K., Newton, Butterworth-Heinemann, 1995, pp. 232-234
- [7] Maupas, H. and Chermant, J. L., "Creep Behavior of a 0-90° SiCf-MLAS Composite", *High-temperature ceramic-matrix composites I, Ceramic transactions*, 57, Westerville, American Ceramic Society, 1995, pp. 369-374

- [8] Bodet, R., Bourrat, X., Lamon, J., Naslain, R., "Tensile Creep Behaviour of a Silicon Carbide-based Fibre with a Low Oxygen Content", *J. Mater. Sci.*, 30, 1995, pp. 661-677
- [9] Curtin, W. A., "Theory of mechanical Properties of Ceramic-Matrix Composites", *J. Am. Ceram. Soc.*, 74[11], 1991, pp. 2837-45