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Microstructure of Tyranno ZMI fiber Reinforced Carbon Matrix Composites after Partial Oxidation at Different Temperatures

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ABSTRACT

Tyranno fiber and tyranno fiber coated with CVI derived carbon reinforced carbon matrix based composites(ZMI29 and ZMI30) were oxidized in the partial pressure of oxygen at different temperatures. Microstructures of the composites were studied after oxidation by SEM and XRD. It was observed that the oxidation in partial pressure of oxygen occur in active regime. The CVI derived carbon interphase reduces the rate of oxidation and protects the tyranno fibers from early degradation to certain extent. The decomposition of fibers in these composites initiated at above 1000°C particularly ZMI29 based. The decomposition rate of tyranno fibers in selective oxidation is higher in ZMI 30 composite which ultimately damages the fiber morphology. Therefore, there was greater possibility of degradation of fiber properties in these composites. However, continuous oxidation under partial pressure of oxygen protects the fibers from damages by the formation of silicon dioxide protective film.

Key Words: Tyranno fibers, Composites, Microstructure, Partial oxidation.

1. INTRODUCTION

Continuous ceramic fibers reinforced ceramic matrix composites are exhibit attractive properties such as low densities, high elastic modulus, and high strength at elevated temperatures. Thus, they are considered as high potential materials for various field of applications including engine components and reentry thermal protection for spacecrafts [1,2]. One of the main advantages of ceramic matrix composites with respect to conventional carbon/carbon composites and non-oxide ceramic matrix composite is their better oxidation resistance [3]. On the other hand non-oxide ceramic matrix composites have limitation due to its oxidation in oxidizing atmosphere as low as temperature 500°C with the formation of gaseous oxides [4]. The oxidations of fiber-matrix interfacial layers in non-oxide ceramic matrix composite strongly affect the mechanical properties [5].

The thermal stability of silicon carbide fibers depends upon their structure and morphology. The bulk SiC is decompose at above 2000°C, it is stable compound up to very high temperature in an inert atmosphere. However, polymer (polycarbosilane) derived Nicalon SiC based fibers (Si-C-O) are thermodynamically unstable and it decomposes at high temperature >1200°C [6,7]. It compose of amorphous silicon oxycarbide (SiCxOy), SiC crystallites and free carbon, when heated these fibers in an inert atmosphere above 1200°C, the SiCxOy phase decomposes into SiC crystal and then generate both SiO and CO gases. To overcome decomposition problem of Nicalon based SiC fibers, the reduction of oxygen, namely from the SiCxOy phase is effective in improving the thermal stability of these fibers. Therefore, Hi –Nicalon was developed with a low oxygen content by curing with electron beam irradiation [8]. These fibers have excellent thermal stability even at 1500°C. Another method for improving the thermal stability is the use of a suitable coating to restrict the outward transport of decompose gases. In particular , a SiO_2 film produced by oxidation treatment is very effective in retarding the decomposition reaction of Nicalon and Si-Ti-C-O fibers (Tyranno , Ube industries Co. Tokyo, Japan) [9,10].

But the tyranno Si-Ti-C-O fibers at high temperature, easily transfer to TiC crystal and suffer extreme damage following the contact with the salts [11,12] Therefore, to overcome this problem Si-Ti-C-O fibers, Ube industries are developed the Tyranno ZM and ZMI fiber by replacing the titanium by zirconium. These tyranno ZM fibers with oxygen content 10 wt. % and tyranno ZMI (Lox-M) with 7.6 weight % of oxygen have much higher thermal, oxidation and chemical-corrosion resistance [13]. In the present study 3D woven composites used are made of tyranno ZMI fibers. The objective of the present study to understand the effect of partial pressure of oxygen on microstructure of tyranno ZMI fiber reinforced carbon matrix and tyranno ZMI fiber coated with CVI derived carbon fiber reinforced carbon matrix composites during oxidation at different selective temperatures.

2. EXPERIMENTAL

In the present investigation Tyranno ZMI fibers based 3D orthogonal composites were used for the oxidation studies under the partial pressure of oxygen at different temperatures.

Tyranno ZMI fiber contains Si , Zr ,C and O (Ube Industries Ltd., Japan). The chemical composition of tyranno fiber by weight percentages are Si 56.6 , C 34.8, O 7.6 and Zr 1.0. The two type of 3D orthogonal composites were used with fiber volume fractions of 0.19, 0.19 and 0.02 in the x, y and z directions respectively.

(i) Tyranno ZMI fiber reinforced carbon matrix (ZMI 29) and

(ii) Tyranno ZMI fiber coated with CVI derived carbon (interphase of thickness ~ 0.5 to 0.7 (μm) reinforced carbon matrix (ZMI30). The carbon matrix used in these composites derived from a phenolic resin.

The oxidation studies of composite were carried out by thermo gravimetric analysis (TGA, model STA-449C. Netzsch, Geratebau, Selb, Germany) under partial pressure of oxygen. The rectangular shape composites specimen of size 10 mm x 5 mm x 4 mm (weight of ~ 500 to 700 mg) was placed in alumina crucible in a such way that the maximum area of composites exposed to the gas pressure. The two type of gases were used during the experiments. The pure argon gas (99.99 % purity) with 0.1% of oxygen due to impurities and argon- oxygen gas mixture contain 1% of oxygen, both the gases were allowed to flow from the bottom of the furnace at flow rate of 100ml/min. Heating rate of 10°C/min was kept constant during heating and cooling cycle. The controlled oxidation was carried out at different temperatures T,(500°C<T<700°C),(900°C<T<1000°C), (1200°C<T>1400°C) (1350°C<T<1500°C) and (RT <T<1500°C). During oxidation initially all the sample heated up to an initial oxidation temperature in argon gas and also cooled after final oxidation temperature under the atmosphere of argon gas to room temperature. The microstructure of composites before and after oxidation was characterized by scanning electron microscope (SEM model S-4700, Hitachi Ltd., Tokyo, Japan). The composites were studied for structural changes occur due to oxidation by XRD with a Cu-Kα radiation under conditions of 40 kV and 200 mA and scan speed 0.1/min. (Model RINT2500, Rigaku Co., Tokyo, Japan). Both the type of composites oxidized at same conditions between selected temperatures of oxidation was coded as;

Oxidation condition	Composites Code	
	ZMI29	ZMI30
No oxidation	S1	T1
500-700°C in 1% O_2	S2	T2
900-1000°C in 1% O_2	S3	T3
1200-1400°C in 1% O_2	S4	T4
1350-1500°C in 1% O_2	S5	T5
RT-1500°C in 1% O_2	S6	T6
RT-1500°C in Air	S7	T7

3. RESULTS AND DISCUSSION

3.1 Oxidation Studies by TGA

Figure 1(a) shows the TGA curve of composites after oxidation up to 1500 °C in air and argon gas having 1% oxygen content. These curves are coded as S6 , T6, S7 and T7 which are given in details in section 2.

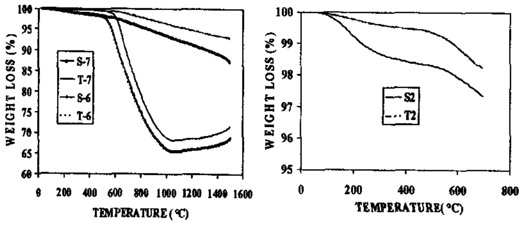

Fig.1a **Fig.1b**

Fig.1(a): Weight loss observed during oxidation in Air and Argon gas with 1% O_2 ;(b): During oxidation in between 500-700°C in argon gas with 1% O_2.

Weight loss pattern divided in three region. In first region the weight loss up to 500° C, in second region up to 1000°C and third region up to 1500°C in both the composites. The weight loss in both types of composites up to 1000°C is due to the oxidation of carbon matrix and carbon interphase. Rate of oxidation in S6 and T6 composites increases with increasing temperature and rate of oxidation is comparatively lower in case of T6 composites, due to higher thermal stability of the CVI derived carbon interphase because of its structure. Which ultimately contribute to the reduction of weight loss occur due to oxidation. This continues weight loss with increasing temperature indicates, the oxidation take place in partial pressure of oxygen is so called active oxidation in both the type of (S6 and T6) composites by continues gasification. However, oxidation in air shows the weight gain after 1000°C in both composites. The rate of oxidation is suddenly an increase after 500°C, which is continues up to 1000°C. After 1000°C thermal decomposition of amorphous phase of fiber started and rate of oxidation is decreases by the formation SiO and then SiO_2. After 1100°C, weight gain is observed in both the composite up to 1500°C. Thus oxidation take places also called as passive oxidation in composites (S7 and T7) but weight gain and the total weight loss is comparatively lower in T7 composites. Figure 1 (b) shows the weight loss occurs at temperature in between 500-700°C in argon gas having 1 % oxygen in S2 and T2 composites. In both the composites weight loss up to 500°C increases slowly and above 500 to 700°C, a rapid increase in weight loss is observed and this difference in ultimate value of weight loss is due to the carbon interphase. In case of T2 composites oxidation is inhibited due to the higher thermal stability of CVI derived carbon interphase and lower value of porosity. The apparent porosity in S1 composite is 6.2 % and in T1 composite 2.5 % which is measured by Archimedes principle, where distilled water is used as liquid medium.

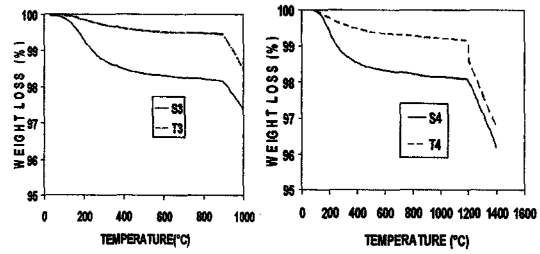

Fig.1c **Fig.1d**

Fig.,1(c): Weight loss observed during oxidation in between 900-1000°C in argon gas with 1% O_2;(d): During oxidation in between 1200-1400°C in argon gas with 1% O_2

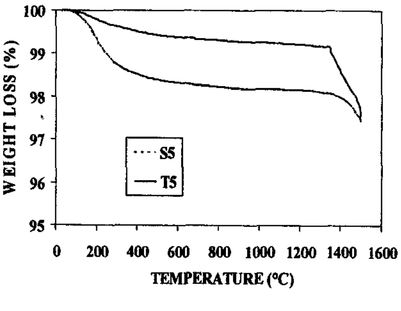

Fig.1e.: Weight loss observed during oxidation in between 1350-1500°C in argon gas with 1% O_2.

The weight loss up to 900°C increases slowly in argon gas pressure, after 900°C, the weight loss is in the partial pressure of oxygen increases suddenly in both composites. The sudden weight loss is a result of higher rate of oxidation due to sudden incorporation of oxygen pressure at high temperature and as a result of an increase of rate of gasification of carbon. Figure 1(d) shows the weight loss occurs in between the 1200 to 1400°C composites. The weight loss up to 1200°C increases slowly in argon gas pressure, after the incorporation of partial pressure of oxygen. A sharp increase in weight loss is observed in case of T4 composite as compared to S4 composites. The sharp weight loss in T composites might be due to the sudden reaction occurring between oxygen, phenolic resin derived carbon and CVI derived carbon as well as at high temperature decomposition of tyranno fibers. It is interesting to note that gap between the two curves decreases at 1200°C suddenly. Figure 1(e) shows the weight loss occurs at temperature in between the 1350 to 1500°C. In the same way weight loss increases in argon gas flow as observed in fig. 1(d). After 1350°C weight loss increases in both composites but the behavior of weight loss curve is different. It shows that the rate of oxidation is higher in T5 composites as compared to S5 composites. As observed above, oxidation in air, the degradation of fibers started after 1000°C and as a result weight gain is observed. However in the partial pressure of oxygen; a continuous weight loss is observed above 1000°C in all the cases. This is due to the higher rate of gasification of carbon as compared to the formation of SiO_2 from SiC which contributes towards the weight gain. However, in case of T5 composite at temperature of 1500°C, weight loss is almost similar as in S5, this can be due to the degradation of fibers by higher gasification of SiO in T5 composites. This phenomenon is limited to the exposed cross section of composites sample due to partial pressure of oxygen. In all these cases of selective oxidation, oxidation is occurred in active regime because of continues gasification of carbon from the matrix phase, even though there is a thermal decomposition of fibers by the formation of SiO_2 film.

3.2 XRD results after oxidation of composites

Figure 2 shows the XRD pattern of ZMI29 composites (S) after oxidation at various temperatures in partial pressure of oxygen. Initially without oxidation of ZMI29 composites, the XRD pattern of ZMI29 composites consist of peaks at 2θ= 24.40 of carbon, at ~35.2, 42.9, 60.16, and 71.24 of amorphous SiC (curve S1). Upon oxidation under partial pressure of oxygen at temperature in between 500-700°C, peaks appear at little higher value of 2θ (curve S2). With increasing oxidation temperature the changes occurs in the structure of carbon as well as fibers. On oxidation in between the 900-1000°C, additional peak appears at 2θ= 21.50, at very low intensity value is of amorphous SiO_2 (tridymite). This shows that oxidation of tyranno fiber is initiated at above 1000°C (curve S3) under partial pressure of oxygen. In oxidation between 1200-1400°C, SiC peak shifted to the higher value 2θ, which is due to amorphous phase transform toward crystalline. Also a decomposition of tyranno fibers which results in the formation of SiO_2, a peak of SiO_2 appears relatively at higher intensity (curve S4). After the oxidation between 1350-1500°C, sharpness of SiC and SiO_2 peaks increases and is of SiO_2 cristobalite (curve S5). This is due to the crystallization of SiC and SiO_2 with increasing temperature. At oxidation in partial pressure of oxygen from room temperature to 1500°C, the appearance of strong peak at 2θ= ~22 of cristobalite SiO_2 and peak of SiC at higher value of 2θ is due to the crystallization during oxidation with increasing temperature. The new additional peaks are observed which are of cristobalite SiO_2 (curve S6). But on oxidation under air, the intensity of SiO_2 and SiC peaks increases and are shifted to little lower value of 2θ.

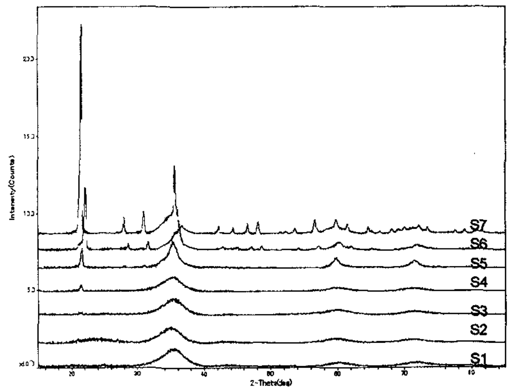

Figure 2: XRD pattern of oxidized ZMI29 composites

Figure 3 shows the XRD pattern of ZMI 30 composites (T) after oxidation at various temperature in partial pressure of oxygen. Initially T1 composites consist of peak at 2θ= 25.40° of carbon and other peaks of SiC (curve T1). If we compare the S1 and T1 curves, the peaks appeared at higher value of 2θ, indicates that the fiber-matrix bonding also changes the structural parameters of individual component. The higher value of carbon at 2θ= 25.4 is due to the carbon interphase derived from CVI. On oxidation in between 500-700°C, carbon peak appeared at higher value of 2θ = 25.49 (curve T2) is might be due to the carbon derived from the phenolic resin which is consumed in the oxidation process. On the other hand after oxidation in between the 900-1000°C, the carbon peak appears broadened at 2θ= 24.994° (curve T3) and peak of SiO_2 is not registered in this case. However, in the similar condition it is register in S3. This shows that the structure of CVI derived carbon changes due to oxidation,. After oxidation, between 1200-1400°C (curve T4), the SiC peaks are shifted to the higher value and appears sharper. An additional peak is observed due to the degradation of tyranno fibers by the formation of SiO_2 at 2θ =21.55° of tridymite. However, oxidation in between 1350-1500°C, the sharpness of all the peaks increases and SiO_2 phase transform from tridymite to cristobalite (curve T5). CurveT6, after oxidation from room temperature to 1500°C under the partial pressure of oxygen, the very strong peak of SiO_2 at 2θ= ~22°, is of SiO_2 cristobalite, as well as the peak of SiC appears at higher value of 2θ due to transformation of amorphous to crystalline SiC. This shows that the crystallization of SiC and SiO_2 occurs in this temperature range. Curve T7 is after oxidation in air up to 1500°C. It consists of SiO_2 cristobalite and crystalline SiC but it appears at comparatively lower intensity. On comparing the curve S7 and T7, it indicates that, the quantitative presence SiC and SiO_2 is higher in case of S7 composites.

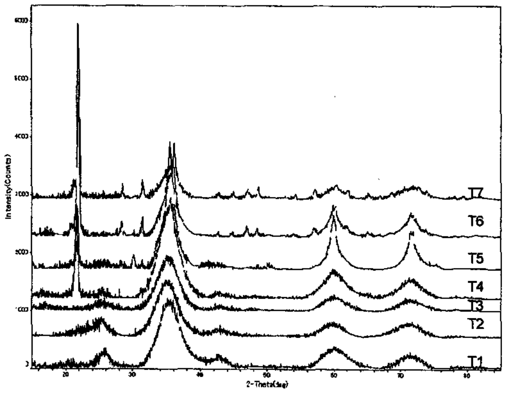

Figure 3: XRD pattern of oxidized ZMI30 composites

3.3 Microstructure of composites after oxidation

Figure 4 shows the scanning electron micrographs of S and T composite surfaces after the oxidation at different temperatures. In case of S1, the fibers are well bonded with carbon matrix and in T1, CVI derived carbon layer around the tyranno fibers and between CVI carbon layers, matrix carbon in which open porosity is visible. After oxidation, in case of S2, the annular gaps around the fibers are generated due to oxidation at fiber-matrix interface while in T2 composite; matrix is oxidized between the CVI carbon layers as shown in Figure 4 (T2). However, oxidation in between 900-1000°C, oxidation progresses in matrix region as well the gaps around the tyranno fibers enlarges as shown in S3. In T3, the oxidation progresses in side the composites and partly carbon interphase is also oxidized. The oxidation initially takes places at the matrix region which progresses in side the composites up to certain depth (may be maximum up to open porosity channel), thereafter there is a oxygen diffusion towards the carbon interphase with increasing temperature and (at critical temperature) the gasification of CVI derived carbon initiated. The oxidation of CVI interphase takes place from inwards to upward direction which shown in figure 4c (T3). Also the appearing of annular gap between CVI interphase and fibers is due to oxidation at fiber-CVI carbon interface.

On oxidation in between 1200-1400°C, in case of S4, partial degradation of the tyranno fibers that resulted into the formation SiO and then SiO_2 which is deposited on carbon matrix surface to some extent as shown in figure 4d (S4). On the other hand, the oxidation in case of T composite, takes place though matrix and then carbon interphase by oxygen diffusion. It is observed during oxidation in between 900-1000°C the oxidation of carbon interphase is initiated at higher temperature through inside oxidized matrix phase in x- directionally oriented fibers because at first the matrix carbon is oxidized. Therefore, at higher temperature the oxidation of tyranno fibers occurs through inward direction of fibers where the CVI carbon is oxidized, as a result the oxidation of tyranno fibers is initiated by oxygen diffusion with the formation of SiO, CO and the SiO_2, that deposited on the CVI derived carbon interphase and hence CVI interphase is protect from oxidation at the same time. The oxidation of interphase and fibers are temperature dependent. At temperature typically above about 950°C, the formation of SiO_2 that deposited on interphase, can block the channels through which oxygen enter, there by preventing further oxidation of interphase. However, oxidation in x-directionally oriented fibers occurs in different way. The fibers are exposed in two directions, cross section and length direction, in length direction the matrix is oxidized easily because more matrix area expose to oxygen directly as compared to matrix available in y-directionally oriented fibers surface. In this case the oxidation via gasification of CVI interphase takes place easily because ingress of oxygen from two directions, direct reaction of oxygen with horizontally placed fibers surface and ingress of oxygen through the z-directionally oriented matrix porosity pockets. Thereafter, oxygen reacts with fiber surface and as a result evaporation of SiO and CO that result in porous surface of fibers with some deposition of SiO_2. But due to partial pressure of oxygen and strong affinity of oxygen toward carbon, the sufficient oxygen is not available for the formation of SiO_2 film. As a result higher weight loss is registered in composites T as compared to S due to evaporation of SiO and CO, which leads to the formation of porous fiber surface as shown in figure 4 (T4-1). Figure 4 (T5 and S5) shows the scanning electron micrographs after oxidation in between 1350-1500°C. In this case the oxidation of carbon matrix as well as tyranno fibers by formation of SiO and then SiO_2 which deposited on the fiber surface, also there is the formation some SiC needle like crystal this attributed to the thermal decomposition of tyranno fibers from inward direction in both the cases in y directionally oriented fibers while the surface of the fibers protected by SiO_2 film. In this temperature range SiO_2 phase transition occurs from amorphous to slightly crystalline, this effect is more in case of T5 composites as compared to S5. In S5 the appearance of smooth SiO_2 film is due to the amorphous structure of SiO_2. On the other hand the x directionally oriented fibers is protected from the film in S type of composites as shown in figure 4, S5-1. The extent of decomposition of fibers in T5 composite may be higher which resulted in degradation of fiber morphology.

Figure 4 (S6 and T6) shows the micrograph after oxidation from room temperature to 1500°C under partial pressure of oxygen. In S6 and T6, the SiO_2 is deposited on fiber surface, and the SiO_2 film is thicker as compared to S5 and T5. Also the cracks observed in film are due to the transformation of amorphous SiO_2 to crystalline cristobalite and as a result decreases the volume of SiO_2 film during cooling from the oxidation temperature to room temperature due to the difference in coefficient of thermal expansion of SiC and SiO_2. The tensile stress might be generated across the SiO_2 film and fiber interface. This leads to produce the cracks in the SiO_2 film [14]. Figure 4 (S7 and T7) shows the SEM after the oxidation in air. In S7 composites SiO_2 film is deposited on the surface of fibers, cracks appears in the SiO_2 film but the crack are little different than observed in S6 and T6. This may be due to the less crystallization of SiO_2 film in these composites, as a consequence lower volume shrinkage. Also there is bonding between the SiO_2 film, this may be due to the reduction of diffusion area [15]. However, in T7, deposition of film on fibers with growth of needle like SiC crystallite is just initiated in the film. In this case the degradation of fiber morphology is comparatively less than what observed in T4 and T5 composites micrograph. The SEM observation is in agreement with observation made by TGA and XRD.

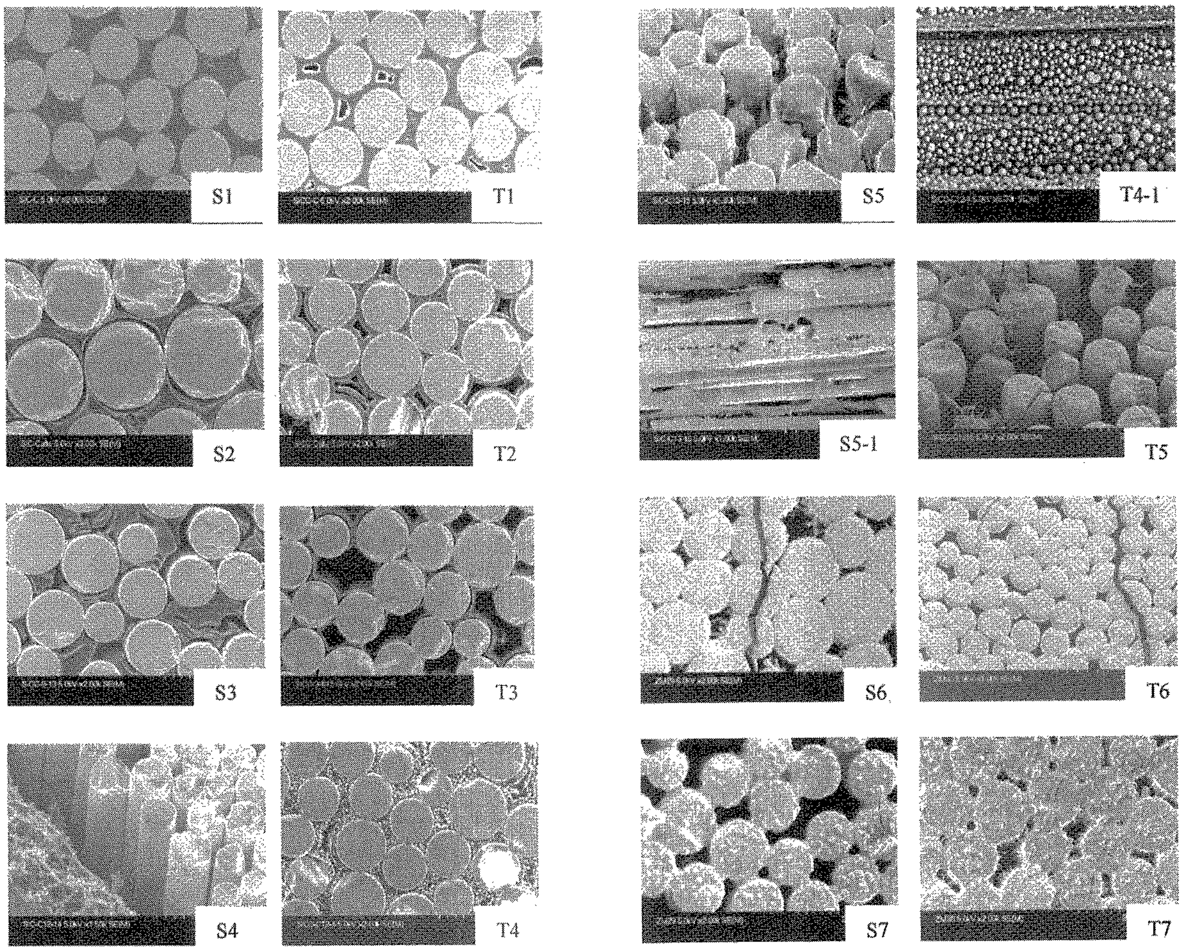

Fig.4: Scanning electron micrographs of composites before and after oxidation.

4. CONCLUSIONS

The oxidation of composites in the partial pressure of oxygen is a complicated process. The oxidation is limited and localized in non-oxide ceramic matrix composites. The oxidation of fibers in these composites is initiated at above 1000°C particularly in ZM29 based. The CVI derived carbon interphase reduces the rate of oxidation and protects the tyranno fibers from early degradation to certain extent. But decomposition rate of tyranno fibers in selective oxidation is higher in CVI derived carbon coated interphase non-oxide ceramic matrix composite which ultimately damages the fiber morphology. Therefore, there is a greater possibility of degradation of fiber properties in these composites. However, continuous oxidation under partial pressure of oxygen protects the fibers by formation of silicon dioxide protective film and oxidation occurs in active regime.

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