DEFORMATION PROCESSES OF CMCs AND THEIR MATRIX SKELETONS

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Abstract

The deformation of ceramic matrix composites (CMC) is controlled by several processes, occurring in the matrix phase, in the enforcing phase or at the interface between them. For the separation of deformation controlling processes matrix phase skeletons as measuring samples have been prepared by chemical elimination of other constituents (elemental silicon, reinforcing C fibers and amorphous carbon phases) from C/C-SiC composites. C/C-SiC structures prepared by liquid silicon infiltration of 2D woven fabric and chopped fiber bodies were studied. Bending stress – strain curves were measured for C/C-SiC samples and their SiC skeletons. Processes dominant in stages of deformation could be identified by comparing stress – strain curves for CMC bodies and their skeletons.

Keywords: CMC, carbon fiber reinforcement, SiC skeleton, bending test

INTRODUCTION

Ceramic matrix composites (CMCs) promise new, beneficial combinations of characteristics. They offer the advantages of ceramics, for instance high thermal resistance and excellent wear resistance together with an improved level of their unfavorable properties, for instance unreliability or rigidity [1-3].

It is rather difficult to understand the mechanical behavior of CMCs. Several phases constitute, not only their characteristics and shares affect the mechanical properties but the strength of interfacial bonds and the geometrical arrangement of phases, as well [2-6]. The measured strain - stress curves in most cases contain different stages [3,4,7,8] suggesting sudden changes of the dominant deformation process. It is thought that the description of processes participating in the deformation could be easier if some mechanical parameters together with microstructure would be determined for respective phases. We worked out a method to study the matrix skeleton by extracting the other phases. The examined CMC was carbon fiber enforced silicon carbide which might be a usable materials for brake discs and brake pads [2,3]. In this letter our first results are presented.

EXPERIMENTAL

Materials

The C/C-SiC composites studied in present paper were prepared by liquid silicon infiltration of carbon fiber reinforced carbon martix preforms.

Starting materials: Two types of reinforcing carbon fiber structures, a 2D woven fabric (Sigratex 2D, KDK 8043 from NOVIA Hungary) and a chopped fiber of Toray HT 3k

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with length of 5-10 mm were used as variants. For the preparation of the C_f/C prepregs commercially available phenolic resins from BAKELITE AG-Germany were used. Silicon for reaction bonding was applied as Silgrain, $d \approx 0.2 - 2$ mm, from Elkem GmbH, Germany.

Two variants were used at the fabrication process. Variant I. A number of fabric layers circular in shape, were stacked together. Warm pressing with resins, curing and pyrolisis in N_2 atmosphere formed the carbon matrix of the C_f/C prepregs. Siliconization was carried out in carbon crucible under vacuum. Variant II. Chopped fibers mixed with resins were transferred into circular mould. Carbonization and siliconization was carried out similarly as described above. Chemical composition of the produced samples is given in Table 1. The produced composite tablets (diameter $\sim$ 56 mm, height $\sim$ 5.1-5.5 mm) were cut by diamond saw into bars of 5x3.5x50 mm³.

Tab.1. Chemical characterization of bodies with C/C-SiC structures

Sample	Type of reinforcement	Si [weight %]	C [weight %]	SiC [weight %]
210	2D textile	5.1	46.3	48.5
195	2D textile	1.1	48.5	50.4
221	short fiber	3.7	47.6	48.7
263	short fiber	2.1	43.0	54.9

Processing route of the SiC skeleton bodies

The non-reacted Si content of the selected C/C-SiC composite bars were chemically etched in $HF:HNO_3:H_2O = 1:1:1$ etching mixture at room temperature overnight. After washing with purified water and drying the carbon phases (fibers and amorphous) were eliminated by oxidation under air at 1100ºC for 20 hours. The remained SiC skeleton was passed then for physical investigations. The time parameters of the processing route were empirically determined by systematic weighing control and are not independent of the dimensions of the bars and the porosity of the CMC.

EXAMINATIONS

The microstructure of samples was studied by scanning electron microscopy, SEM with a JEOL-JSM25 and a JEOL-JSM 840 microscope.

The mechanical properties were measured at room temperature using four points bending with spans of 40 mm and 20 mm, the speed of the cross-head was 0.5 mm/min. Young's modulus was calculated from the initial part of the load vs. bend curves using a best-fit method. Time-stress curves were measured on the same samples till the fracture without direct measuring of bend, the time of deformation was approximately proportional with the strain. Both samples „as reaction bonded by Si infiltration" and after chemical removal of non-reacted Si, amorphous C and C -fiber constituents were examined.

RESULTS AND DISCUSSION

Having completed the chemical elimination of Si and C constituents from the precursor CMCs various SiC products differing in macro and micro-morphology were resulted. Products from precursor composites with incomplete silicon infiltration, or with too low amount of SiC content in the composites disintegrated by the end of the processing route. The majority proved to be a body pseudomorphous in outer shape with its precursor having a solid spongy structure (Fig.1) and able to be handled with tweezers and moreover subjected to bending examinations. These bodies are denominated as skeletons during this study.
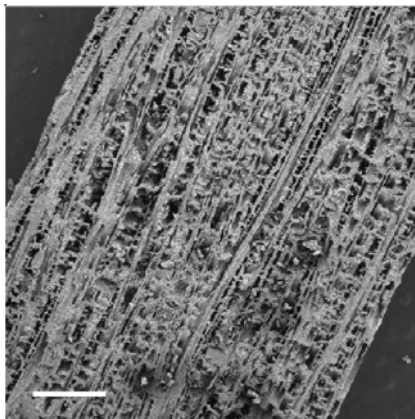
Fig.1. SEM micrograph. Bar: 1 mm. General view of SiC skeleton produced by chemical removal of Si and C constituents from a bar cut from a 2D woven C fiber reinforced SiC composite tablet. The examined surface is perpendicular to the plane of textile.
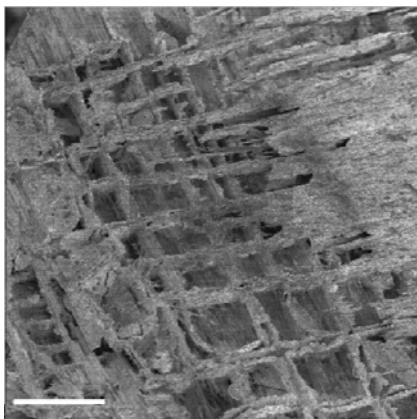

Fig.2. SEM micrograph. Bar: 100 μm. Top view of SiC skeleton produced by chemical removal of Si and C constituents from a bar cut from a 2D woven C fiber reinforced SiC composite tablet. Under a relatively compact SiC layer SiC crystallized pseudomorphous to the structure of the precursor C-fiber textile structure. Note high pores in shells of SiC walls rectangular in shape indicating that firstly formed SiC layers preserved bulks of C-fiber bundles from the attack of elemental silicon.
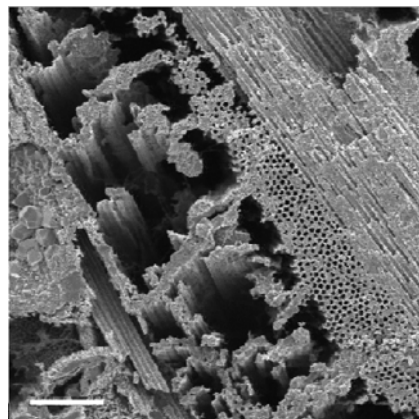
Fig.3. SEM micrograph. Bar: 100 μm. View perpendicular to the textile planes in the composite precursor of SiC skeleton. Layers consisting individual tubular pores which are located inside of SiC shells are in sequence with layers characterized by big pores. Note that the layers of the tubular pores formed from individual C-fibers are perpendicular to each other as they were in the precursor 2D woven fabric. SiC particles on the left side of the micrograph show the morphology of crystallites typical for those formed from amorphous carbon during liquid silicon infiltration.

SEM micrographs of typical skeleton surfaces parallel and perpendicular to the basic 2D textile plane are shown in Figs.2-3. The main feature of the SiC skeleton is the

pseudomorphology with the precursor carbon-fiber (bundle) structure. This micromorphology indicates that SiC phases crystallizing during liquid silicon infiltration represent a barrier against aggressive silicon melt in excess. Pores in the structure can be divided into two groups. Small tubular pores (Fig.3) origin from individual carbon fibers wetted by silicon melt and covered by a layer of crystallized SiC. After oxidative elimination of carbon from the cores of fibers SiC shells are left. Big pores (Figs.2 and 3) origin from unattached bundles of carbon fibers. In the case of such bundles the Si melt was not able to penetrate at the beginning of the infiltration and later the fully siliconized outer fibers form protective barrier for the inner part of the fiber bundle.

Fracture surfaces of skeletons produced from 2D woven- and short fiber precursor composites are shown in Figs.4 and 5. Note that high pores, typically present in the skeletons of woven fabric composite samples, cannot be found in the fracture surface of the "short fiber" skeleton.
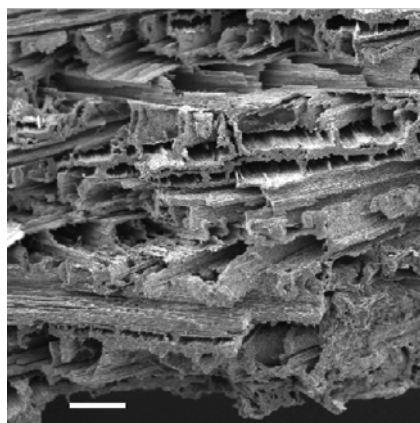

Fig.4. SEM micrograph. Bar: 200 μm. Fracture surface of SiC skeleton (Sample 210) produced by chemical removal of Si and C constituents from a bending test bar cut from a 2D woven C fiber reinforced SiC composite precursor.
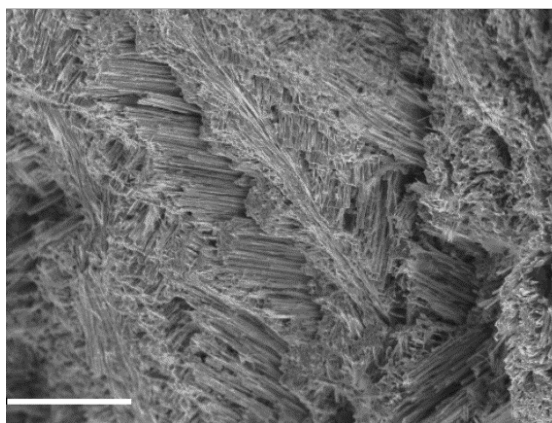
Fig.5. SEM micrograph. Bar: 100 μm. Fracture surface of SiC skeleton produced by chemical removal of Si and C constituents from a bending test bar cut from a short fiber reinforced SiC composite precursor. The skeleton fibers are oriented and show symptoms of laminarization indicating the effect of hot pressure, a processing step at the fabrication of the composite.

The measured Young's modulus values are given in Table 2. Figures 6,7 and 8, shows a few examples measured on materials having different micro-structures.

Tab.2. Young's modulus of composites and skeletons.

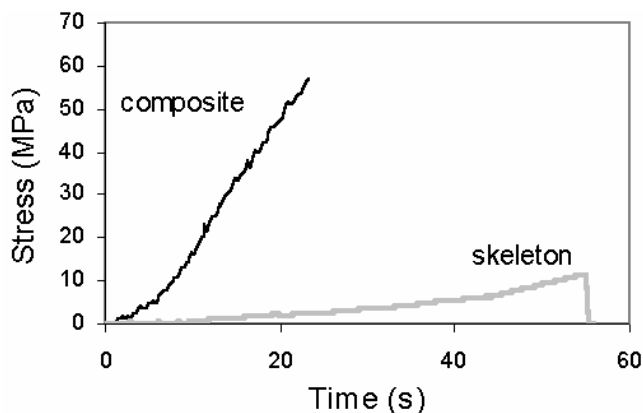| Sample	Type of reinforcement	Composite [Gpa]	Skeleton [Gpa]
210	2D textile	35.0	28.5
195	2D textile	19.3	6.9
221	short fiber	61.2	19.1
263	short fiber	12.6	Small

Fig.6. Bend strength as a function of the time of the displacement of the cross-head. SiC skeleton produced by chemical removal of Si and C constituents from a bar cut from a 2D woven C fiber reinforced SiC composite tablet (Sample 210). Both curves have elastic-rigid character, no obvious interaction between them is visible.

In the case of sample 210 the difference between moduli was relatively small (Table 2), suggesting that modulus of the skeleton phase was larger than that of carbon containing phase. At higher reductions both curves are straight lines (Fig.6), this behavior is typical for ceramic materials. The elongation of skeleton was 0.052 % (equivalent to 55 s). The composite had a smaller elongation, 0.019 %, meaning that the carbon containing phase and the silicon carbide broke simultaneously.
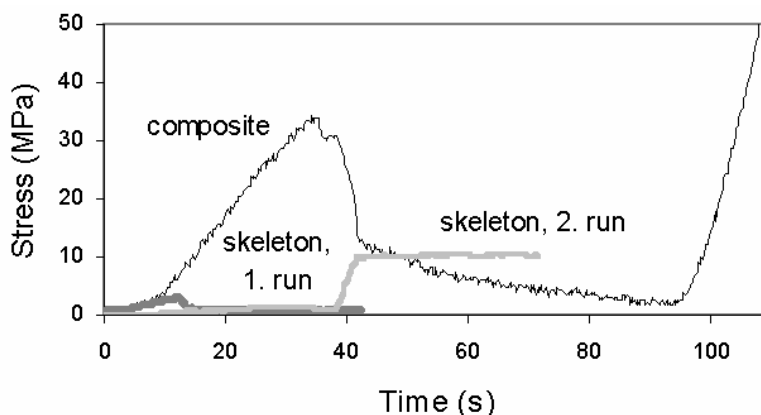

Fig.7. Bend strength as a function of the time of the displacement of the cross-head. SiC skeleton produced by chemical removal of Si and C constituents from a bar cut from a 2D woven C fiber reinforced SiC composite tablet (Sample 195). The break point of the curve of the skeleton at 35 s (about 0.033 % strain) coincides with the drop of stress of the composite.

In sample 195 the modulus of carbon containing phase is higher than that of skeleton (Table 2). This sample as well as sample 210 contained woven fibers; their time-stress curves, however, differed (Fig.7 compared to Fig.6). Both curves contained rising

and descending stages. The curve of skeleton contained two horizontal stages where the stress was nearly constant. The second stage started at 35 s (about 0.033 % strain), the curve of the composite began to descend at the same strain, reflecting the effect of structural change of SiC on the properties of carbon containing phase. In this material the redistribution of stress took place three or four times, the clarification of details requires further examinations.
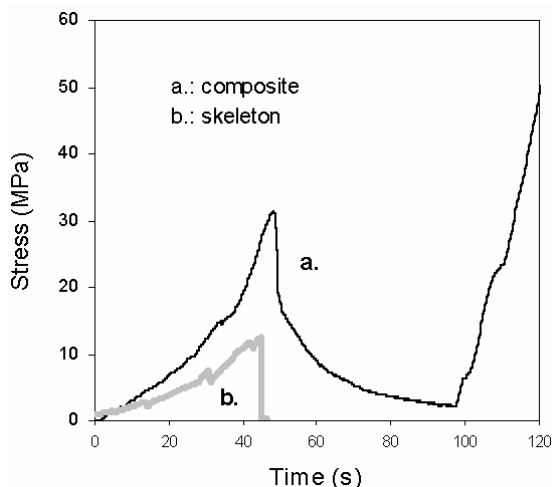

Fig.8. Bend strength as a function of the time of the displacement of the cross-head. SiC skeleton produced by chemical removal of Si and C constituents from a bar cut from a short fiber reinforced SiC composite precursor (Sample 221). At 45 s (about 0.043 % strain) the skeleton breaks, the composite softens.

Samples 221 and 263 were reinforced by short fibers. Modulus of composite 221 was relatively high suggesting that the carbon containing phase was dominant. The character of the curve of composite (Fig.8) is not of ceramic type, this fact also suggests a stronger effect of carbon fibers than in materials with woven fabric. The skeleton breaks at relatively small strain 0.043 % (45 s); this process seems to be responsible for the drop of stress of composite. The mechanical values of sample 263 were smaller than that of 221; its skeleton was very weak, the mechanical properties could not be measured. The orientation of fibers (Fig.5) may cause these displeasing properties.

SUMMARY

A new method was developed to obtain complementary information on processes taking place during deformation of ceramic matrix composites. SiC matrix skeletons were derived from C/C-SiC samples by chemical removing Si and C constituents. Bending stress – strain curves were taken on the C/C-SiC samples and their skeletons. The appearance of bending stress – strain curves measured on composites and their skeletons may be explained by the interaction of SiC skeleton and carbon fibers. In short fiber reinforced composites the carbon containing phase controlled the deformation of SiC phase. In 2D woven fabric reinforced composites firm skeletons were found by SEM and rising and descending stages of deformation could be observed.

Acknowledgement

REFERENCES

[1] Hüttinger, KJ., Greil, P.: cfi/Ber. DKG, vol. 69, 1992, p.445
[2] Krenkel, W., Heidenreich, B., Renz, R.: Adv. Eng. Mat., vol. 4, 2002, p.427
[3] Gadow, R., Speicher, M.: SAE Technical Paper, No. 2003-01-11178
[4] Evans, AG., Zok, FW.: J. Mat. Sci., vol. 29, 1994, p.3857
[5] Ando, K., Chua, MC., Matsushita, Sato, S.: J. Eur. Ceram. Soc.,vol. 23, 2003, p.977
[6] Herzog, A., Vogt, U., Woetting, G.: Key Eng. Mat., vol. 206-213, 2002, p.923
[7] Haruvy, Y., Liedtke, V. In: 2nd Int. Meeting on Space and Aerospace Materials Technology, Seibersdorf, 2002, p.7
[8] Singh, RN.: Lecture at 8. ECERS, Istanbul, 2003, paper 364