

Experimental Investigation of Multifunctional Interphase Coatings on SiC Fibers for Non-Oxide High Temperature Resistant CMCs

M. Tsirlin, Y. E. Pronin, E. K. Florina, S. Kh. Mukhametov, M. A. Khatsernov
SRC of RF GNIChTEOS, Moscow
H.M. Yun
NASA Glenn Research Center, Cleveland, OH
R.Riedel, E. Kroke
Technische Universität, Darmstadt

1 Introduction

Interphase coatings are necessary constituents of ceramic matrices/ceramic fibers composites (CMC). They provide high fracture toughness and prevent a catastrophic destruction of the essentially brittle materials. The interphases for non-oxide high temperature CMC intended for a long-term work in oxidizing environments (HTI) have gone a long way of development. Starting from monolayered adhesion controlling coating of carbon with working temperature up to 350-400°C, they were improved to analogues BN coating fit for temperatures up to 600-700°. The work on alloying BN with Si [1] seems gave the possibility to raise the temperature of exploitation up to 1000-1100°C and to enhance the oxidation and hydrolysis resistance.

Nevertheless this level is not enough for the hot units with oxidizing environment in aviation engines [2]. High temperature (1300-1400 °C) and long-term work (thousands of hours) at cycling thermo-mechanical conditions, which are inevitable in this application, put forward especially high demands to HTI. A prolonged stability of the adhesion control and a fibers protection against the oxidation, connected with matrix cracking at the loading, should be ensured. So much attention is paid to more complicated two-layered structure. It is also necessary to take into account, that economic and technological aspects of CMC production dictate the first turn application of thin fibers in tows such as Nicalon, Hi-Nicalon, Hi-Nicalon S, Tyranno, Sylramic etc., which are very sensitive to oxidation and processing of coatings. So the preservation of fiber strength during deposition is a serious problem. The protection of uncoated fiber ends in the composite, formed by machining, should be considered as a separate problem. All these problems are not overcome until now.

According to the theoretical model [3] the strength of a brittle fiber with a brittle coating is an inverse function of "layer thickness to fiber diameter" and "Joung module coating to fiber" ratios. The critical thickness of layer (until the strength of fiber begins to fall down) is about 1,5 % of fiber diameter at the second ratio ~1. Thus a dense layer with a strong adhesion on thin fibers with diameter 11-14 µm should have the thickness no more than 0,15-0,25 µm and so make it very problematic to succeed in putting regular fully dense coating. The experimental data for SiC/B/W monofilaments gave rather good support to this theory. But in thin fiber processing even layers of low modulus materials (BN, E=90 GPa) on SiC base fibers (E=250-400 GPa) decrease the strength sufficiently. The detail experimental data [4]

discovered a surface damage of fibers after staying in the gas components of BN CVD at about 1000°C, 1-10 kPa, 1 min (due to recrystallization in Ar, corrosion in BF₃ and depletion of free carbon in NH₃). The formation of a dense oxide film (E=120 GPa) of about 0,5 μm on the fiber surface in preoxidation prevents the gas evolving after the internal pyrolysis [5] but reduces considerably the strength after oxidizing because the action of oxide layer, irregular oxidizing of free carbon and other surface damages.

The intensive study during the last years gave evidence that the protection of main components of HTI against the oxidation is more complicated problem, than it had been postulated [6]. The comparison of many Si-, Ti- or B-based high oxidation resistant nonoxide materials is shown in Fig.1 [7,8,9 et al.]. They all form dense meltable at middle temperatures oxide layers (SiO₂, TiO₂, B₂O₃ or mixtures of them) – a barrier for O₂ penetration inside the bulk material. Si-based compounds demonstrate very close data for the resistance, depending mainly on the kind of processing. The CVD SiC has nearly the best properties. The reported data for SiBN₃C [10] are very interesting but have yet no confirmation. Even the slowest oxidation can form on SiC at 1300–1400 °C a limited SiO₂ layer (about 0,5 micron) during 6–10 hours. So any protective layer can succeed only to decelerate the oxidation of fibers and the major protective role goes over to the matrix. So the self-healing of cracks in the matrix under the influence of mechanical and thermal stresses becomes a very important technical task. Ceramics of Si-B-N-C type [11,12] are of great interest in this aspect as well.

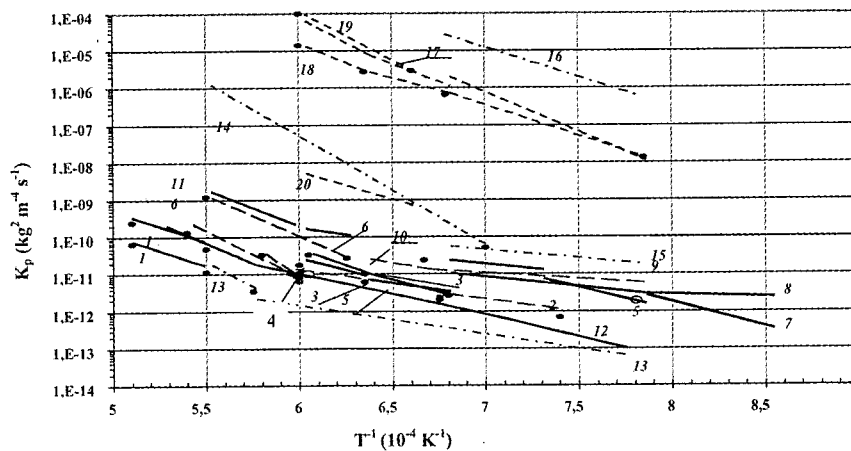


Figure 1: Oxidation kinetics of nonoxide ceramic materials [7,8,9 et al.]: 1-8: SiC; 9: TiSi₂; 10: TiC; 11: MoSi₂; 12: Si₃N₄; 13: SiBN₃C; 14: NiAl; 15: Si; 16: Ti; 17-20: Ti₃SiC₂. CVD, PLS, HP, 7- via PCS, O-monocrystalline, metals (other materials) for comparison

The stability of HTI adhesion control demands also a new solution. Carbon disappears after 400-500°C in air and opens the way for oxygen inside CMC. BN evaporates at 800-900 and melts in the interval 900–1100°C. Other Si, Ti, B-base materials form dense melting oxides at the work temperatures too. Being good for oxidation protection oxides harm adhesion stabilization and fiber strength at cycling temperatures.

Above considerations have led the authors to a more complex (three layered) but technically more radical principal scheme of interphase for HT-CMC. The layer on the fiber surface should be porous with low shear strength to control the adhesion and compensate the CTE difference between the fiber and the next layer. The second layer should be a protective

one. It ought to be dense and high oxidation resistant. The third layer is analogous to the first one to control the adhesion between the protective layer and the matrix. What is especially important and obligatory: both the first and the third layers should not change (melt, dissolve or evaporate) for long periods of cyclic exploitation.

The reality of theoretical structure and detailed positive and negative properties of used components could be evaluated only after an experimental study. So the authors are carrying out systematic experimental work with a scope of perspective components in order to combine an appropriate structure for HTI. In this paper experimental results on coating Hi-Nicalon fibers with MoSi_2 and Si-B-N-C as protective layers and Ti_3SiC_2 as adhesion controlling layer are represented. The all three compounds are objects of intent attention in the researches of HT- materials field during last ten years.

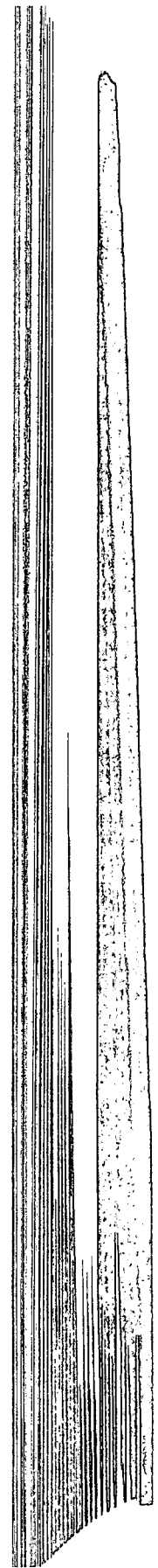
2 Experimental Procedure

The vertical vacuum hot walls reactor was used for putting interphase coatings by CVD and RVD in continuous and stationary conditions in vacuum, Ar, H_2 and N_2 environments. The cylindrical graphite heater formed the constant temperature zone of 200 mm length for the temperature up to 1400°C . There are the reel out and reel up units (for continuous work) and the fiber and plate specimens holder (for fabricating discrete specimens). The installation was provided with the equipment for measuring and transportation of gas mixtures, condensation and absorption of the waste gases and the temperature measurement. The concentrations of vapors were controlled by the temperature in evaporators. The temperature in the furnace was measured by the IR-pyrometer and was calibrated with a thermocouple before the run.

The Mo-Si protective layers were fabricated by CVD + RVD two-stage process on Hi-Nicalon monofilaments and tows. Mo-foil and SiC/C monofilaments of $140\ \mu\text{m}$ diameter were used as model objects. The mixtures of hydrogen with MoCl_5 were used for molybdenum layers and with SiCl_4 – for their following siliconizing by RVD. The layers of $0,1$ to $0,7\ \mu\text{m}$ were fabricated on Hi-Nicalon, up to $2-3\ \mu\text{m}$ – on SiC/C filaments and up to 20 micron - on Mo-foil. The conditions: the temperature of Mo-deposition - $700-800^\circ\text{C}$, of Mo-Si (siliconizing) – $850-1050^\circ\text{C}$, the pressure – 1- 5 kPa and the vapors concentrations about 1 mol. % for MoCl_5 and 2-30 % mol. for SiCl_4 in hydrogen.

Ti_3SiC_2 layers were fabricated by CVD. To create the possibility for element and phase local analyses the first experiments were carried out in stationary conditions on graphite plates $180 \times 12 \times 2$ mm and Nicalon tows fixed together in the working zone of furnace. The coatings had the thickness of 100-300 micron after two hours run on graphite or on the preliminary SiC layer of 5-10 microns. Then the process was realized on Hi-Nicalon fibers at continuous conditions (about 3 m per run) providing the coatings of about 0,5-1 micron after two and five minutes runs. Me_2SiCl_2 , MeHSiCl_2 and HSiCl_3 were used as the source of Si (the first two of them - as the source of C also), CH_4 and CCl_4 – as the source of C, TiCl_4 – as the source of Ti with the ratio Ti:Si:C = 3:(1 to 3): (0,5 to 2). The ratio of reagents to H_2 was about 1:(10-17).

The PIP Si-B-N-C coatings were put over Mo-Si coating or directly on the filaments in N_2 box, equipped with horizontal tube furnace. The Hi-Nicalon tows were impregnated with polymer solutions in TGF, n-hexane, toluene or xylene (concentration 0,02 to 2 mas. %). Then tows were dried, heat treated at $800-1000^\circ\text{C}$ and cooled with the furnace (2 to 5 cycles). PCS and two types of PBCSZs with initial ratios of Si/B = 2 and 3 were used [11].



Thermostability and oxidation resistance tests of fibers were carried out in the horizontal furnace with the graphite tubular heater with the alumina tube enclosed. It was possible to work with vacuum, N₂, Ar and air environment. Temperatures 1200 to 1400°C and times of heating 1.5, 5, 9 and 20 to 60 hours were used. Nicalon and Hi-Nicalon S were also tested at times for comparison. The changing of specimens appearance and structure were the main criteria of oxidation resistance. The tensile strength before and after the heat-treatment was evaluated by Instron machine testing. Specimens were analyzed by optical microscopy, SEM, EPMA, ESCA, WDXA, XRD and AES.

3 Results and Discussion

3.1 Mo-Si coating by CVD

The Mo-foil siliconized at 1200°C formed two-layered coating of about 14 μm in sum. The ratio Si/Mo (at. %) = 1,80–1,75, which is close to MoSi₂, was detected by SEM-EPMA from the coating surface to 8–9 μm deep, then it fell sharply to 0,56 (close to Mo₅Si₃) near 14 μm deep and then became close to zero. These data correspond well with ones of the RVD of porous aluminum preform [13]. The Mo-coating on SiC/C monofilaments was regular up to thickness of 1,0–1,5 micron and had only very slight tendency to defoliation under mechanical impulses. The WDX spectrum (Camebax) detected only molybdenum. The coating siliconized at 1200°C was like the coating on Mo-foil. The thinner (950°C) layer had other characteristics. The data of Camebax analysis for main elements Si, Mo and O (C was counted for 100% balance) in Table 1 showed the depletion of the coating in two layers. The Mo-layer adjoins the fiber surface, above a Si-O layer is located. The oxygen is absorbed most likely by porous Si-layer on the surface. These data gave real evidence that silicon and molybdenum up to 950°C do not form a monolayer of a molybdenum silicide.

Table 1: Local concentrations of the main elements in the points across the Mo-Si coating on SiC/C (950°C/CVD) fibers (at. %%).

Location	Mo	Si	O	C	Sum
Fiber	0.02	45.52	0.45	54.02	100.0
First layer	71.52	3.47	2.91	22.10	100.0
Outer uneven material	5.45	54.61	1.25	38.69	100.0

The layers of Mo and Mo-Si on monofilaments in the tow looked dense and regular, were 0,1 to 0,3 micron (Fig.2a,b). There were no places with weak adhesion to native fiber surface, cracks and sticking fibers together. Increasing the temperature and time made the layers thicker but cruder and creasing and the cracks appeared. AES gave evidence of Mo-layer having thickness of 0.2 – 0.5 micron against a background of Si, C and O. Signals of Si and C probably arose from underlayer material of fiber, oxygen located as usually close to the surface. For the Mo-Si-coatings (Fig.2c) there were a thin (about 20–50 nm) Si-O layer on the very surface, then Mo-layer aligning to the native fiber surface (Fig.3a). The heat treatment at 1400°C in N₂ to initiate a reaction between Mo and Si gave no positive results: Mo-layer disappeared substituted by SiO₂-layer of 200–250 nm thick (Fig. 3b). So these results also show, that there are no MoSi₂ or other chemical Mo-Si compounds in the coating.

3.2 Si-C and Si-B-N-C coating by PIP-technology

One or two impregnations were enough to form coating thickness of 0,2-0,3 micron (Fig.2d). The regular structure had no sufficient defects on the large part of the surface but nevertheless local bulbs were formed in some places even for the most diluted solutions and accordingly for the least thickness. At larger concentrations these bulbs grew, forming pours and sticking of monofilaments. Regular dense two-layered coatings of Mo-Si and Si-B-N-C were fabricated with very diluted solutions of polymer and high boiling solvents. They differed from SiC PIP coatings, which were friable [14].

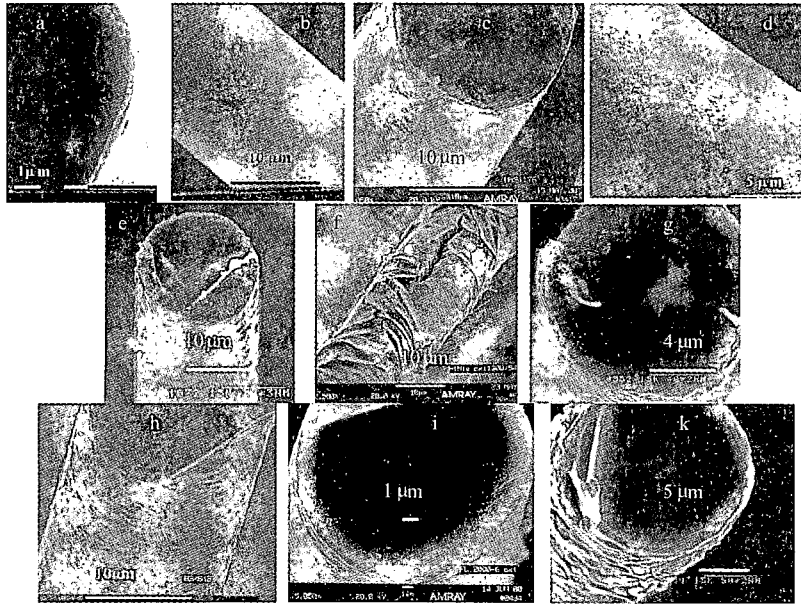


Figure 2: High temperature interphases on Hi Nicalon after the deposition: a,b: CVD Mo; c: CVD Mo-Si; d: PIP Si-B-N-C; e: CVD Ti-Si-C. Oxide layers after 1300°C/20h testing in air on: f: Hi-Nicalon as received; g: with the Mo-Si coating; h: with the Si-B-N-C coating; i: with (Mo-Si) + (Si-B-N-C) coating; k: with Ti-Si-C coating.

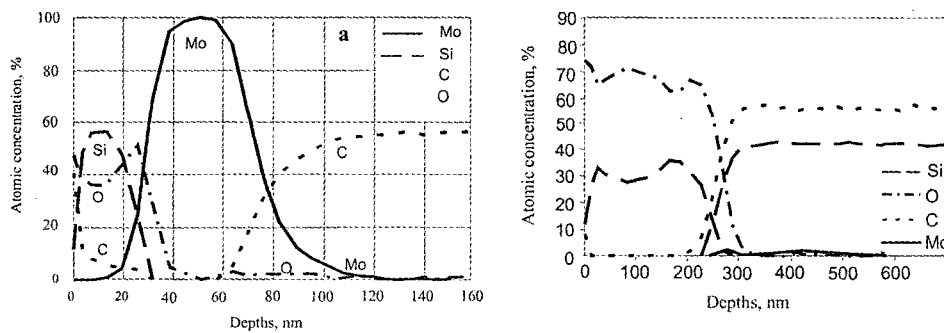
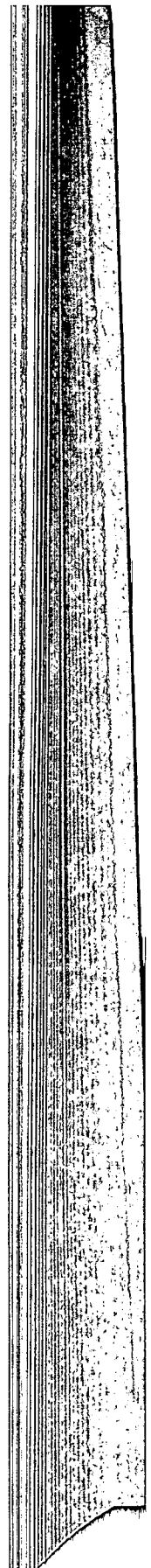


Figure 3: AES data of Hi-Nicalon with the Mo-Si coating before (a) and after (b) heat-treating at 1400°C/20h in N₂



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