Oxidation Behavior of Carbon Fiber Reinforced Silicon Carbide Composites

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Abstract

Carbon fiber reinforced Silicon Carbide (C-SiC) composites offer high strength at high temperatures and good oxidation resistance. However, these composites present some matrix microcracks which allow the path of oxygen to the fiber. The aim of this research was to study the effectiveness of a new Silicon Carbide (SiC) coating developed by DUPONT-LANXIDE to enchance the oxidation resistance of C-SiC composites. A thermogravimetric analysis was used to determine the oxidation rate of the samples at different temperatures and pressures.

The Dupont coat proved to be a good protection for the SiC matrix at temperatures lower than 1240°C at low and high pressures . On the other hand, at temperatures above 1340°C the Dupont coat did not seem to give good protection to the composite fiber and matrix . Even though some results of the tests have been discussed, because of time restraints, only a small portion of the desired tests could be completed. Therefore, no major conclusions or results about the effectiveness of the coat are available at this time.

Introduction

Carbon-Carbon (C-C) composites are a generic class of composites similar to the graphic/ epoxy family of polymer matrix composites. These materials were originally developed for the space program in 1958 by the NASA administration and the U.S. Air Force.[1] These composites offer many desirable characteristics such as tailorable properties, strength and modulus retention at high temperatures, thermal shock resistance, fatigue resistance, low density, good frictional characteristics, low coefficient of thermal expansion, and immunity to natural space radiation. Nevertheless, C-C composites have also proven to be an excellent material not only for advanced aircraft and aerospace applications, but also for numerous common life applications, such as automotive pistons, clutch assembly and brakes for racing cars and even parabolic RF antennas. As previously mentioned, this material offers high strength and stiffness at high temperatures in an inert atmosphere; however C-C composites are easily oxidized in temperatures over 500°C.

Different coats and techniques have been developed to protect the fiber and matrix of C-C composites from oxidizing environments. The most common coats used today are SiC, and Si_3N_4. The most useful techniques used to apply these coats are chemical vapor deposition (CVD) and chemical vapor infiltration (CVI)[1]. Although some material has been published on these techniques many companies are secretive about their manufacturing process. Other published methods that can be found are sputtering, Ion plating, electroplating, and liquid metal transfer which uses TiB, TiC, TiN, Al, Co, and Cu as coats, among others. [1] Even though many reports have been published in this area , it is difficult to compare the results of these investigations due to the difference of their testing environments. In an effort to improve the oxidation resistance of C-C composites Dupont-Lanxide licensed the C-SiC technology from the Société Européenne de Propulsion. This technique combines the high strength of carbon fibers and the good oxidation resistance of the silicon carbide matrix. However, the protection of the matrix is diminished because of the presence of some microcracks in the matrix of the C-SiC composites. These microcracks are a result of the thermomechanical cycles the composites are exposed to during service or manufacturing and they allow the path of oxygen to come into contact with the reinforcement fiber. [2]

The purpose of this research is to study the effectiveness of a Silicon Carbide coat developed by DUPONT-LANXIDE to protect the C-SiC composite in an oxidizing environment. This material (C-SiC composite with the Dupont coating) might be used to protect the lead wing edge and nose cap of the reusable launch vehicle (RLV) under research by McDonnell Douglas, Boeing and NASA. The lead wing edge and nose cap of this vehicle will encounter temperatures ranging from 840°C to 1540°C and pressures between 1 torr and 40 torr.

In order to prove the effectiveness of the coated C-SiC composite, some samples of the material will be exposed to the same temperatures and pressures that the RLV might encounter during entry to earth. A thermogravimetric analysis machine (TGA) will be used to setup an oxidizing environment at the desired pressures and temperatures. The data acquired by the TGA will be used to determine the oxidation behavior of the composites.

Research Project

The composites were developed and manufactured by DUPONT-LANXIDE industries. Three panels were manufactured:

1. 041-02-001 : Uncoated, heat treated.
2. 347-02-197 : Dupont-Lanxide Coated (CVIP) , heat treated as fabric
3. 765-02-014 : Dupont-Lanxide Coated (CVIP) , non heat treated

The same panels were cut in small squares with surface areas that ranged between 6 cm^2 and 7 cm^2, and weighed between 1 gram and 2 grams. The oxidation behavior of the samples were measured by a STA-409 Nezsch TGA/DTA with a computer based data acquisition system.

The flow rate of air was kept constant at 100 sccm. Pressure and temperature were also kept constant during each test. However, different combinations of pressure and temperature were chosen for each test. The combinations were selected to match the entry profile of a future reusable launch vehicle lead wing edge and nose cap (Fig. 1).

A maximum mass loss per surface area of 75 g/m^2 was established for the samples. The C-SiC composites were left to oxidize at the desired pressures and temperatures until they reached a maximum mass loss (target mass loss ,TML) or for a maximum time of 22 hours.

$$TML\ (mg) = \text{Initial Mass (mg.)} - \frac{75\ (g/m2) * \text{Surface Area (cm.)}}{10}$$

A graph of mass versus time was drawn in order to look at the oxidation behavior of the samples (Fig 2 and 3). The oxidation rate and mass loss per time per surface area (g/m^2 min) were calculated. The objective was to verify that the samples would have a maximum oxidation rate of -0.001 g/m^2 min, which would give a service time of 75,000 hrs.

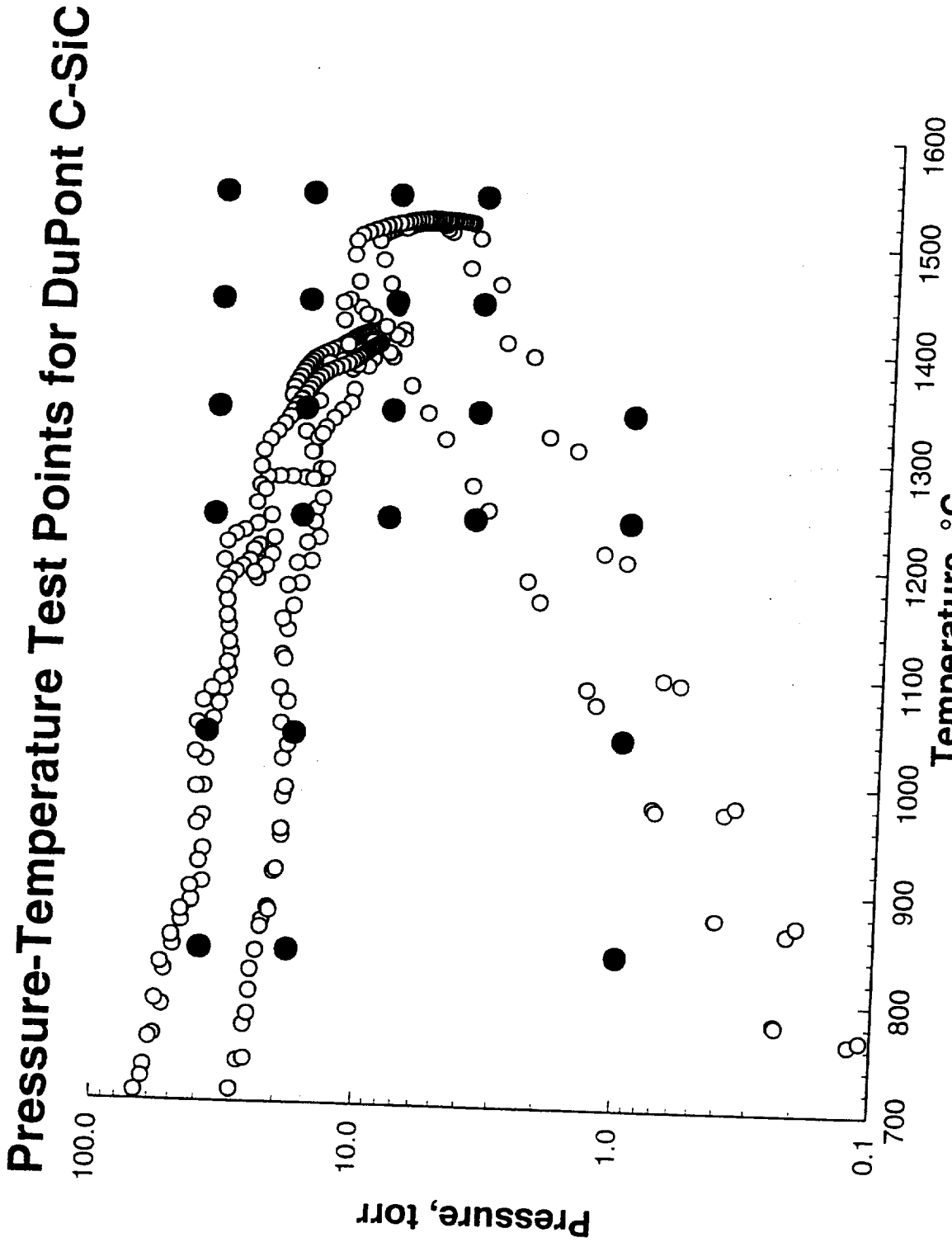
Pressure-Temperature Test Points for DuPont C-SiC
Pressure, torr
100.0
10.0
1.0
0.1
700
800
900
1000
1100
1200
1300
1400
1500
1600
Temperature, °C

Fig 1

Compared Oxidation Behavior of the Same Panel(765) at Different Temperatures and Pressures

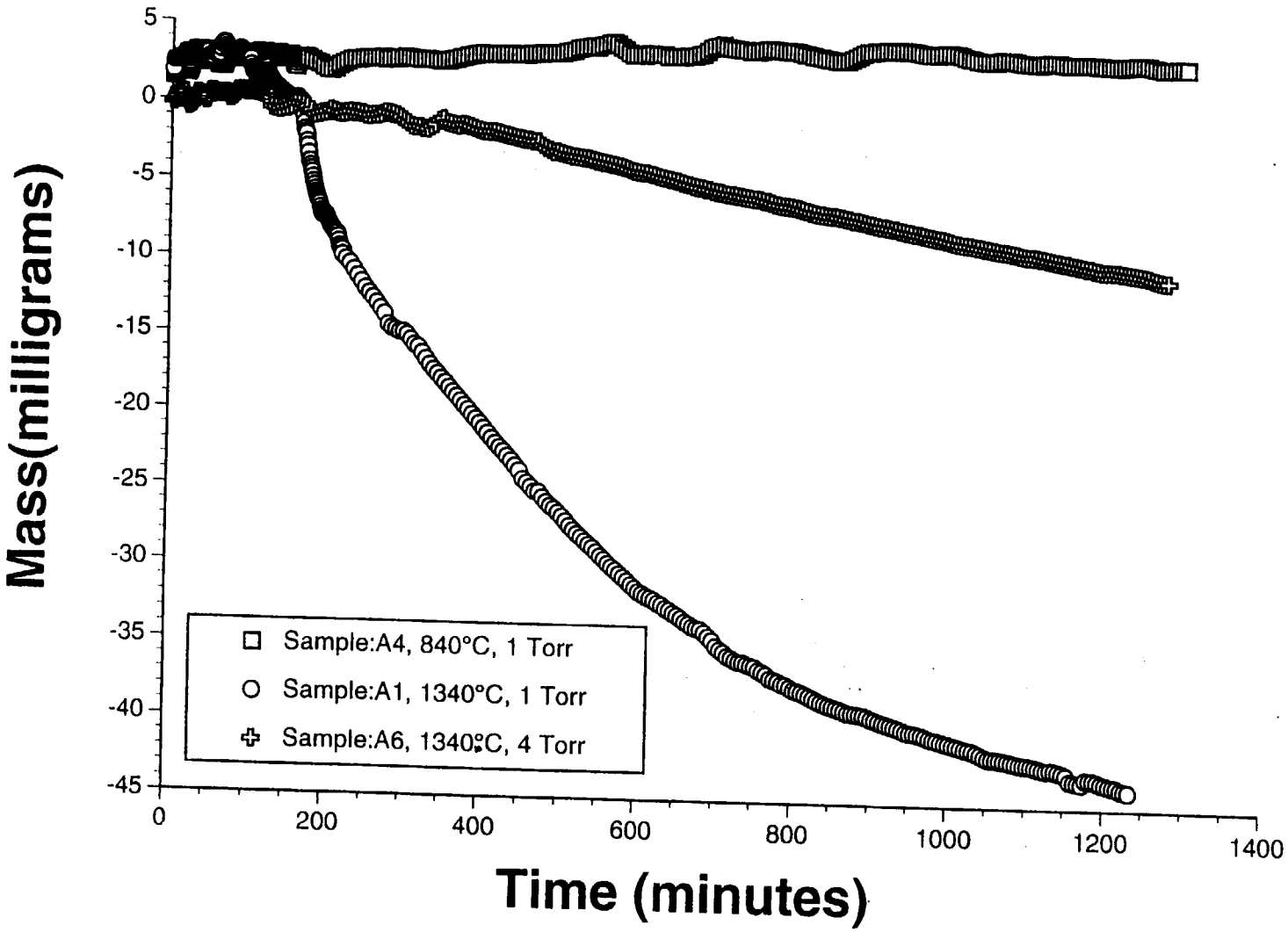

Fig. 2

Compared Plot of the Oxidation Behavior of the Three Panels at the Same Temperature and Pressure

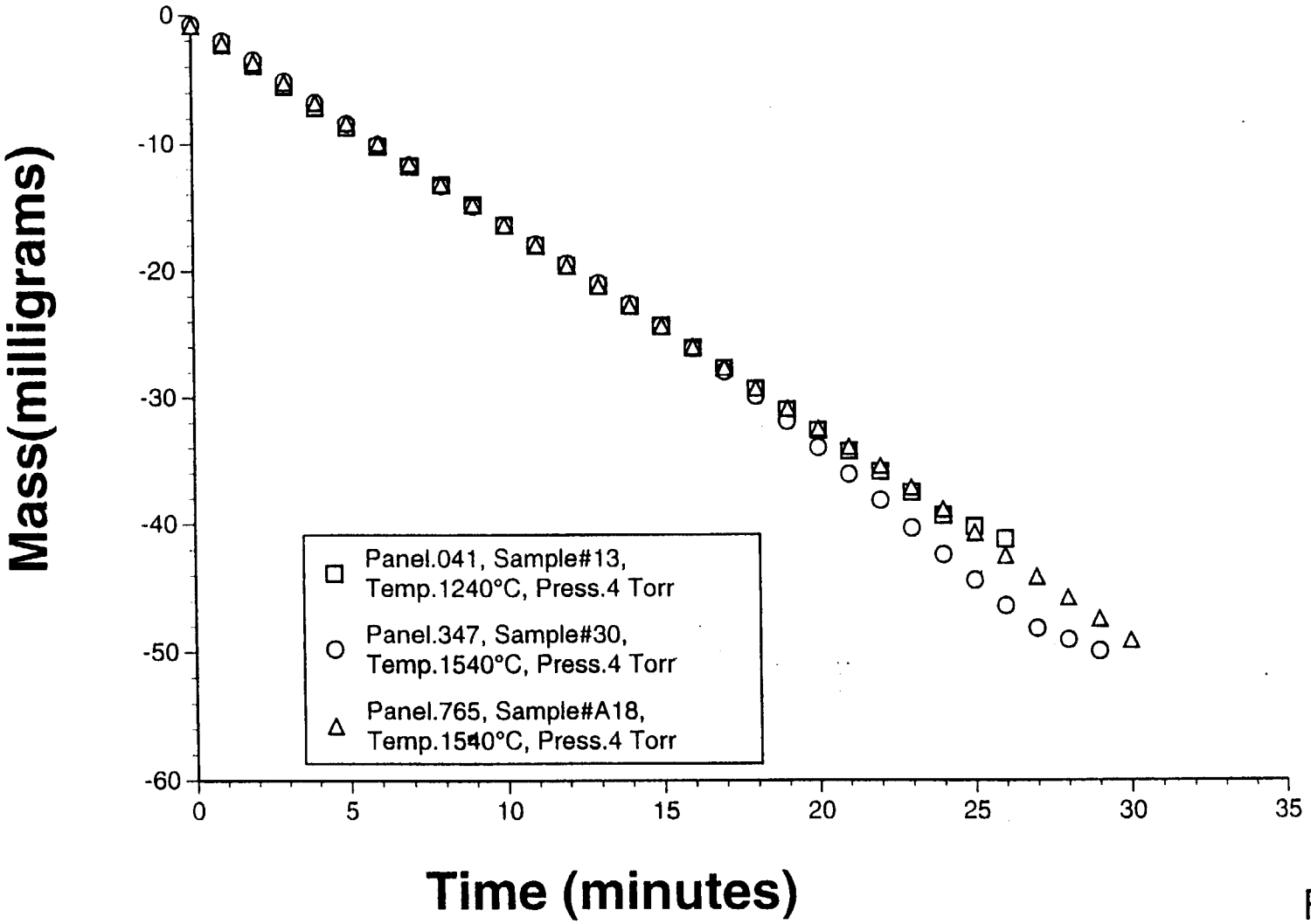

Fig. 3

Results & Conclusion

The Dupont coat proved to be a good protection for the SiC matrix at temperatures lower than 1240°C at low and high pressures (Table 1). On the other hand, at temperatures over 1340°C the Dupont coat did not seem to give good protection to the composite fiber and matrix (Table 1).

Sample	Temperature (°C)	Pressure (Torr)	Areal Mass Change Rate (g/m2 min)
765#A4	840	1	-0.0008
765#A15	840	18.6	-0.0004
765#A21	1040	1	0.0002
765#A23	1240	1	-0.0012
765#A25	1240	4	-0.0007
765#A1	1340	1	-0.0574
765#A6	1340	4	-0.0162
765#A20	1440	4	-0.4267
765#A18	1540	4	-3.5397

Table 1

The thickness of the Silicon Carbide coating might have been reduced during the heat up preparation process of the sample in an inert atmosphere. Because of the low pressures and high temperatures the Silicon Carbide may have encountered its phase change point from solid to gas. The heating process of the sample is not part of the desired environment to test the coat. Because the Silicon Carbide coating may have been lost before starting the test, these results may not be too reliable. It was suggested to repeat the tests at high temperatures by heating up the sample in an oxidizing environment to verify the above mentioned results. Even though some results of the tests have been discussed, because of time restraints, only a small portion of the desired tests could be completed. Therefore, no major conclusions or results about the effectiveness of the coat are available at this time.

References

[1] John D. Buckley, D.D. Edie, *Carbon-Carbon Materials and Composites,* Langley Research Center Hampton, Virginia ,1992

[2] F. Lamouroux, X. Bourrat, R. Naslain,J. Thebault, Silicon Carbide Infiltration of Porous CC Composite for Improving Oxidation resistance ,*Carbon*, Vol. 33 No.4 pp.525-535 ,1995

[3] Wu Tsung-Ming, Wu Yung-Rong, Methodology in exploring the oxidation behavior of coated-carbon/carbon composites, *Journal of Materials Science* Vol.29 pp 1260-1264,1994

[4] Charles M. Earnest, The Modern Thermogravimetric Approach to the Compositional Analysis of Materials, *American Society for Testing and Materials*, Philadelphia,1988,pp.1-18