Improvement in Oxidation Resistance of the Leading Edge Thermal Protection for a Space Shuttle

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To improve the oxidation resistance of a carbon-carbon composite, impregnations were performed using pitches, polyfurfuryl alcohols, and phenolic resins, including a silicon-doped phenolic resin. Oxidation resistance and strength increased for all of the composites as the impregnant-carbon residue increased. The properties of the composites impregnated with the nonsilicon-bearing resins were nearly identical and depended only on the amount of impregnant residue present. However, for equivalent residue concentrations, composites produced with the silicon-bearing resin gave higher strengths and at least 100% better oxidation resistance than was observed for the other composites or for a prototype control material.

Introduction

AN Si-C-coated carbon-carbon composite‡ will be used as the thermal protection for the wing leading edge of a space shuttle.[1] This material is intended to withstand exposure to all environments imposed by earth launch, orbital operation, re-entry, and landing, and to have 100-mission life capability. To insure the reliability of the system, the manufacturer has undertaken to develop a "fail-safe" leading edge which would insure successful completion of a re-entry mission should the oxidation-resistant SiC coat fail. Their approach is to achieve this by increasing the composite laminate thickness from 12 to 34 plies (2.8 × increase) in the stagnation area of the leading edge. Because the oxidation rate of a given carbon tends to increase with time,[2] it can be expected that this increase in thickness will give, at best, a 2.8 × increase in the life of the composite, but at the same time, will impose a weight penalty on the system. Alternative approaches to improving this composite without the weight penalty are desirable.

Two other possibilities have been considered for increasing the oxidation life of the RPP composite without imposing significant weight penalties. The first of these involves improving the pore structure of the composite. The microscopic examination of this material showed it to contain many unimpregnated or partially impregnated pores. Improving the efficiency of impregnation would increase the amount of carbon residue in the pores, decreasing the amount of surface for oxidation, and the need for so many plies.

The second, and more hopeful, possibility for extending the life of the composite is to directly improve its oxidation resistance. This might be achieved by using an impregnant which would form a protective coat within the pores of the composite. Such protection would have an additional advantage over that of increasing the composite thickness. Subsurface oxidation is almost certain to occur as the result of cracking or crazing of the SiC surface coat. Coating the pore surfaces within the composite with an oxidation resistant material could significantly retard this subsurface oxidation.

To explore these possibilities, a series of impregnants and their influence on oxidation behavior was studied. Three classes of impregnants were used: polyfurfuryl alcohols, phenolic resins, and pitches. One phenolic resin contained a silicon group which was expected to convert to SiC on pyrolysis and provide oxidation resistance in the pores. Besides impregnation efficiency and oxidation resistance, flexure strength was determined on all materials.

Experimental

The manufacture of the RPP composite includes the following steps.[1] A graphite cloth, prepregged with phenolic resin, is laid-up, molded, autoclave-cured, and finally pyrolyzed to 800°C. In this condition the composite is designated RPP-0. It is then impregnated three times with catalyzed polyfurfuryl alcohol (PFA) and heat-treated, as before, after each impregnation. At this point the product is identified as RPP-3. An oxidation resistant, SiC coat is then applied at 1700°C by a pack-siliconizing process.

Impregnation samples 4.5 in. long × 0.5 in. wide were cut from a 10 in. × 12 in. sheet of 13-ply RPP-0 composite obtained from the manufacturer. The thickness of the 13 plies was nominally 0.17 in. For comparison, a sheet of RPP-3 was also obtained. Seven impregnants, representing two polyfurfuryl alcohols, three phenolic resins and two pitches, were used. These are described in Table 1. Samples were processed through as many as four impregnation-pyrolysis cycles by methods previously described.[3] Impregnation effectiveness was determined from composite weight-gain after a final 1700°C pyrolysis, and reported as the percentage increase over the original unimpregnated sample weight.

Oxidation resistance was determined with a thermogravimetric analysis (TGA) apparatus[4] on specimens 0.50 in. long × 0.25 in. wide × 13 plies thick, cut from the impregnated samples. These specimens were placed in a nichrome wire basket which was suspended from one arm of the TGA balance in a quartz tube through which 5 SCFH of dry air was passed. The test was begun by sliding a cylindrical furnace, preheated to 730-750°C, into position over the quartz tube, after which the sample took approximately 5 min to reach temperature. Weight-loss was continuously recorded as a function of time until 40% of the original sample was lost.

Flexure strengths were measured by standard ASTM procedures[5] on rectangular parallelepipeds 13 plies thick, 0.250 in. wide, and 1.750 in. long. The load was applied perpendicular to the plies and the warp direction was orientated parallel to the long axis of the specimens. At least four replicate samples of each material, including the RPP-0 and RPP-3 controls, were tested.

Impregnation Effectiveness

Figure 1 shows weight-gain of the RPP-0 as a function of the impregnation-pyrolysis cycle and type of impregnant used. For comparison, an unimpregnated RPP-0 sample was given the same 1700°C pyrolysis treatment and, as expected,

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‡Developed by LTV Aerospace Corporation, Vought Systems Division, and designated both as Reinforced Pyrolized Plastic (RPP) and Reinforced Carbon Composite (RCC).

Table 1 Impregnants

Impregnation series	Manufacturer and grade	Type	Impregnation[a] Viscosity, cP	Temp, °C
I-54	Reichold, Varcum 8251[b]	PFA	400	20
I-56	LASL[b]	PFA	400	20
I-58	Monsanto, SC-1013[c]	Si-Phenolic	3000	65
I-60	Ironsides, FF-26	Phenolic	3000	70
I-62	Monsanto, SC-1008[c]	Phenolic	8000	70
I-64	Allied, 15V	Coal-tar Pitch	800	150
I-66	Ashland, 230SP	Petroleum Pitch	800	150

[a] Impregnation pressure for all samples was 200 psi.

[b] Contained 4 wt% maleic anhydride curing catalyst.

[c] Stripped of its solvent prior to use.

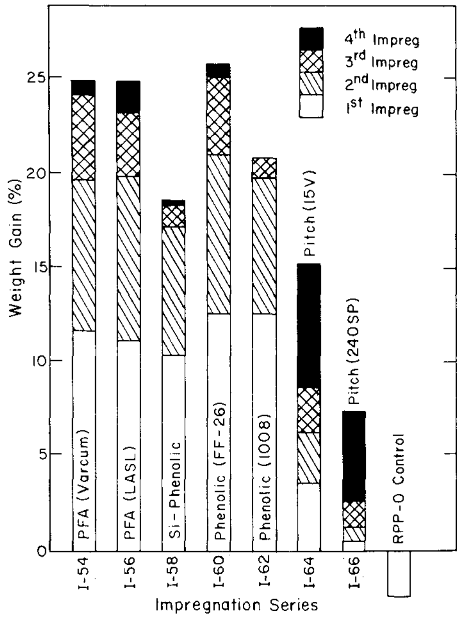

Fig. 1 Composite weight gain as a function of the number of impregnations and impregnant type.

lost weight. The weight-gains for the impregnated samples are not corrected for this loss. The most effective impregnants were the two PFAs and one of the phenolic resins (Series I-60). These produced significantly higher weight-gains than any of the other impregnants. The least effective were the pitches. The poor results here, however, were due almost entirely to the way in which the impregnated samples were processed. It was observed that pitch tended to exude from the pores of the composite during the early stages of pyrolysis, significantly reducing the total weight-gain. This problem was partically overcome for the final pitch impregnations by a post-impregnation chlorine treatment[3] which produced a much higher weight-gain (Fig. 1). The silicon-phenolic resin produced an intermediate weight-gain.

If density increase were the only consideration in the improvement of the RPP composite, the most practical choice of impregnant type would be the polyfurfuryl alcohols. They lead to high weight-gains and, because of their low viscosity (Table 1), are conveniently handled at room temperature. The pitches potentially could give very high weight-gains, provided the chlorine treatment were used, but are inconvenient because of the higher processing temperatures required. Phenolic resins are nearly as easily handled as the PFAs, and give good weight-gains. It will show now, however, that improvement in composite density has a relatively small effect on oxidation resistance compared to that of an oxidation inhibitor in the impregnant.

Oxidation Resistance

The oxidation test used here was not intended to simulate re-entry conditions. It was used principally to provide information on the potential for improving the bulk oxidation resistance of the unsiliconized composite. But since oxidation below the SiC coat can be a considerable problem on re-entry, and is essentially a static oxidation phenomenon, it should be directly relatable to the oxidation behavior observed here.

In Figs. 2a-c weight-loss data vs time in the oxidation furnace are summarized for the RPP composites. Included in these plots are the data for the RPP-0 and RPP-3 control samples, and the time-temperature profile for sample heat-up. The pitches are not included, as they had just a slight build-up of carbon residue, and their weight-loss data occupy only a narrow band between the RPP-0 and RPP-3 curves. Only one set of curves is given for the PFA and phenolic resin types, as they typify the others.

From these data, the curves of Figs. 3 and 4 have been constructed. They show the temperature T_i at which oxidation starts and the time t_{10} at which 10% of the material is lost, as functions of the amount of impregnant residue produced in the composite samples. Figure 3 shows how the type and amount of impregnant residue can influence the initiation of oxidation. At low residue concentrations the phenolic resins, including the silicon-phenolic resin, produced impregnated composites whose oxidation kinetics are inferior to those of composites impregnated with pitch or PFA. Their oxidation initiation temperatures are 20° to 30°C lower. At higher concentrations, however, the oxidation initiation temperatures of the phenolic-impregnated composites increase rapidly and become nearly equal to those of the composites impregnated with pitch or PFA. This early oxidation of the phenolics, however, does not adversely affect their performance beyond the first few percent weight-loss. Considerably more important than the initial loss rate is that at a longer-time.

In Fig. 4 the times to 10% weight-loss for the composites have been compared as functions of the impregnant residue concentration. Here it can be seen that the pitches, phenolic resins and PFAs give comparable performance as impregnants, and although oxidation resistance increases with the amount of impregnant residue, no particular carbon-precursor impregnant is superior to any other. The silicon-phenolic resin, however, is far superior. After four impregnations it offers a significant improvement in oxidation resistance over the others, including the RPP-3 control.

To determine the relative ability of a composite to resist oxidation, the function $R_x = t_{x,s}/t_{x,c}$ was chosen where t_x represents the time required to reach x% weight-loss for the sample, s, or the RPP-3 control, c. As pointed out above, the samples took approximately 5 min to reach temperature, but, from Fig. 2, it is clear that the time of initiation of oxidation may differ from this. The time t_x has not been corrected from the initiation time t_i because in practice the heat-up time during re-entry is part of the total lifetime of the composite. However, correcting the t_x values in the previous function by subtracting t_i would result in greater apparent relative oxidation resistances for the silicone-phenolic-impregnated composites. Thus the expression used to compute R_x is conservative in showing the superior oxidation resistance of these composites.

Using the weight-loss data from Fig. 2, the relative oxidation resistances, R_x, were computed and are shown in

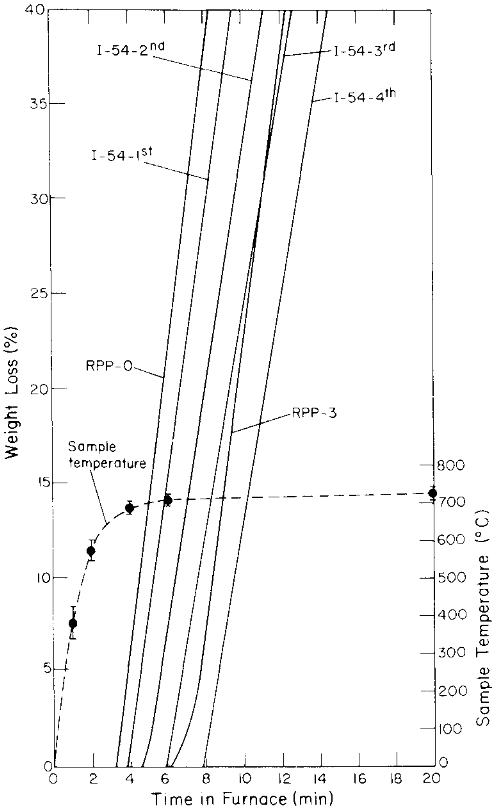

Fig. 2a Oxidation weight-loss vs time in furnace for PFA-impregnated RPP composites (Series 1-54).

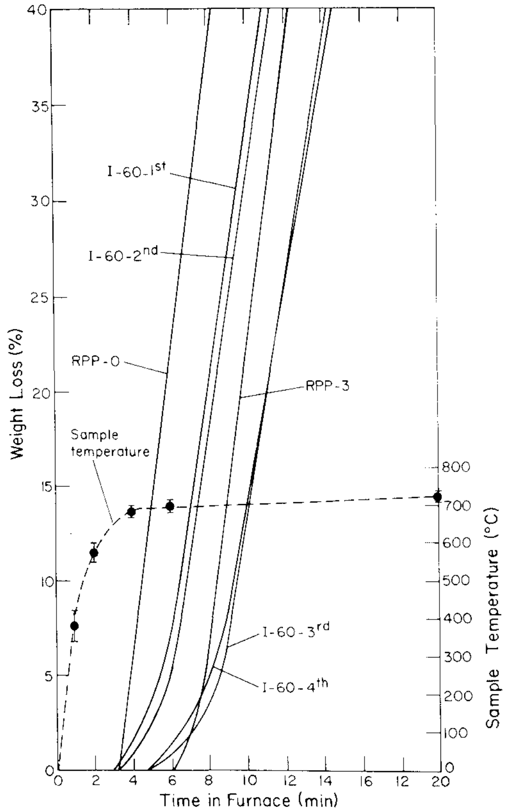

Fig. 2b Oxidation weight-loss vs time in furnace for phenolic-impregnated RPP composites (Series 1-60).

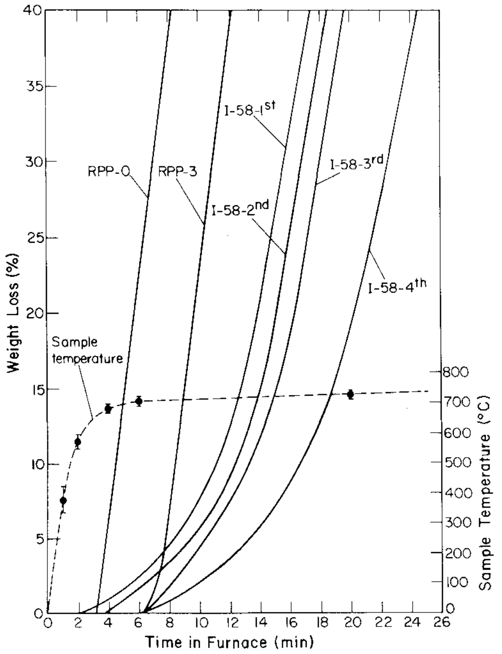

Fig. 2c Oxidation weight-loss vs time in furnace for silicon-phenolic-impregnated RPP composites (Series 1-58).

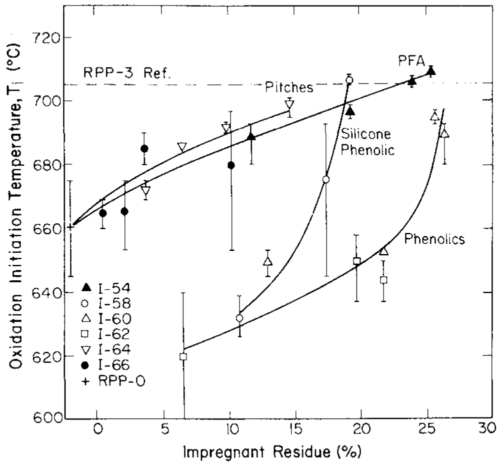

Fig. 3 Temperature, T_i, at which composite oxidation begins vs impregnant residue concentration.

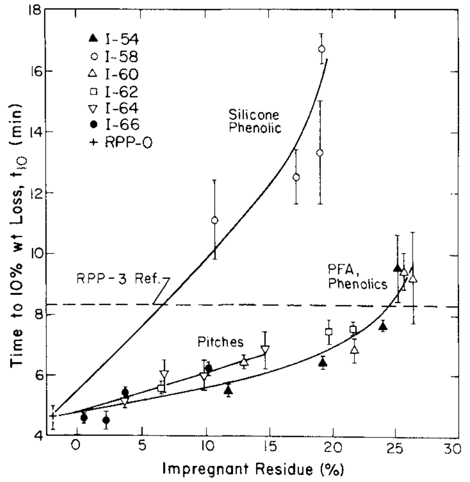

Fig. 4 Time to 10% weight loss, t_{10}, vs impregnant residue concentration.

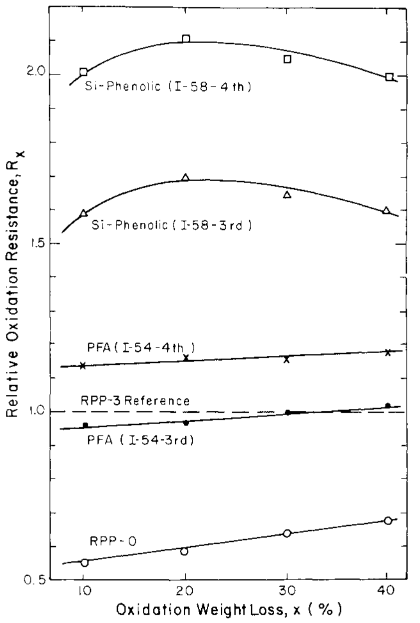

Fig. 5 Oxidation resistance, R_x, of impregnated RPP composites, relative to RPP-3, vs extent of oxidation, x.

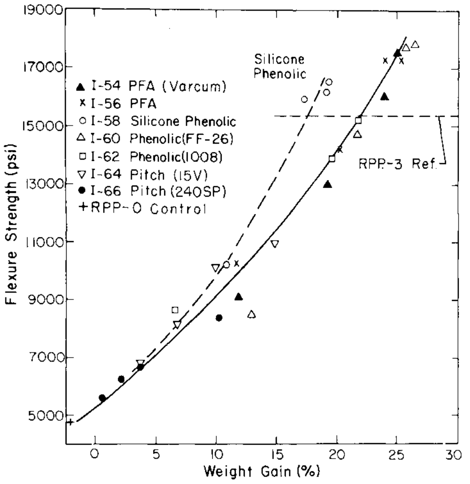

Fig. 6 Flexure strength vs impregnant-residue weight-gain for impregnated RPP composites.

Table 2 Silicon content of impregnated composites

Composite	Impregnant residue, wt%	Silicon content of composite, wt%	Silicon content of residue, wt%
RPP-0	. . .	<0.02	. . .
I-58-1	10.8	0.52	5.3
I-58-2	17.3	0.81	5.5
I-58-3	19.1	0.96	6.0
I-58	19.3	0.98	6.1
RPP-3	. . .	0.02	. . .

Fig. 5 vs the extent of oxidation, x. These curves clearly show the superiority of the silicon-phenolic resin as an impregnant. The composite which was impregnated three times with PFA (I-54-3rd) had an oxidation resistance nearly identical to that of the RPP-3. Whereas the silicon-phenolic resin gave a 60% increase for the thrice-impregnated composite (I-58-3rd) and at least 100% increase for that impregnated four times (I-58-4th). The improvement resulting from this last impregnation was particularly surprising, since the corresponding increase in residue weight and silicon content were almost insignificantly small, as shown in Table 2. Attempts to identify the oxidation inhibiting phase by optical microscopy were unsuccessful.

To evaluate how the strength of the composite is affected by impregnation, particularly by the silicon-phenolic resin, flexure strength was measured on all samples, including the RPP-0 and RPP-3 controls. The average flexure strength is given in Fig. 6 as a function of impregnant residue weight-gain. With the exception of the samples impregnated with the silicon phenolic resin, the strength is related only to the amount of impregnant residue-carbon added to the composite, and not to the type of impregnant used. For the silicon-phenolic resin, however, the strength increased more rapidly with weight-gain than it did for the other impregnants. Two or more impregnations with the silicon-phenolic resin produced a composite stronger than the RPP-3 control. This is shown by the three open circles in Fig. 6 which lie above the RPP-3 reference line. Therefore, for equivalent strengths, the silicon-phenolic resin would provide a lighter composite.

Conclusions

To improve oxidation resistance of the RPP carbon-carbon composite, samples of the unimpregnated RPP-0 were impregnated with three types of materials: polyfurfuryl alcohols, phenolic resins, and pitches. One of the phenolic resins contained a silicon component that was expected to increase the oxidation resistance by the formation of SiC. With the exception of this resin, it was found that improvement in strength and oxidation resistance was essentially independent of the type of impregnant used, and depended only on the amount of carbon residue deposited by the impregnant in the composite. Thus, samples containing the same amount of residue, regardless of source, had the same strength and oxidation resistance. Three impregnation-pyrolysis cycles on the RPP-0 composite, using the PFA and phenolic resins, yielded strengths and oxidation resistances equivalent to those of the RPP-3 control.

For those samples impregnated with the silicon-phenolic resin, a given weight-gain gave a slightly greater strength than those observed for the composites impregnated with the other resins. The oxidation resistance, however, was increased to a disproportionately larger degree. Thus, the composite which was impregnated four times had an oxidation resistance at least twice that of the RPP-3 control. This improvement in oxidation life is almost equivalent to that which would be expected by increasing the RPP-3 composite thickness to the extent proposed by the manufacturer. Three advantages are likely to accrue from increasing the oxidation resistance of the composite rather than its thickness: 1) a net saving weight, 2) a possible smaller change in aerodynamic shape of the airfoil, for a given oxidation exposure, and 3) a retardation of subsurface oxidation.

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