ARC JET RESULTS ON CANDIDATE HIGH TEMPERATURE COATINGS FOR NASA'S NGLT REFRACTORY COMPOSITE LEADING EDGE TASK

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ABSTRACT

In 2000, arc jet testing was conducted on thirteen material systems for possible use on the nose leading edge of the Hyper-X program's X-43A Mach 10 vehicle. Six material systems survived 3, 130-second cycles. To support NASA's Next Generation Launch Technology Programs (NGLT) need for passive refractory composite leading edges with multiple reuse capability at temperatures up to 3600°F, these six materials were subjected to an expanded arc jet test program. This expanded arc jet test program included three phases. The purpose of the first phase was to generate emissivity data as a function of temperature. The purpose of the second phase was to determine if the material systems had any thermal cycling durability, and the third phase was to determine whether the materials could survive an arc jet test of one hour duration. Some of the coating systems were found to have very low emissivities, suggesting that they would not be good candidates for leading edges coating. Other coating systems survived both the second and third phases of the test program and showed potential for use as an oxidation protection coating for leading edges. This presentation summarizes the test program results.

INTRODUCTION

In 2000, arc jet testing was conducted in the H2 arc jet facility at the Arnold Engineering Development Center (AEDC), Arnold Air Force Base, TN on thirteen material systems for possible use on the nose leading edge of the X-43A Mach 10 vehicle. Six material systems survived 3, 130-second cycles. NASA's Next Generation Launch Technology Program has a need for passive refractory composite leading edges that have multiple reuse capability at temperatures up to 3600°F. To further investigate the capability of material systems that survived the AEDC test for use in the hypersonic program, an expanded arc jet test program was planned. This expanded arc jet test program included three phases. The purpose of the first phase was to generate emissivity data as a function of temperature. The purpose of the second phase was to determine if the material systems had any thermal cycling durability, and the third phase was to determine whether the materials could survive an arc jet test of one hour duration. This paper summarizes the results of all three phases of the program.

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RESULTS AND DISCUSSION

MATERIALS

The material systems tested are listed below (Table 1). Initially, material systems from Engelhard, MER, Starfire, RCI and Synterials were supplied for testing. Due to the time separation between the first phase testing and the second and third phase testing, one new substrate and two new coatings were added to the test matrix. The Engelhard, MER and Synterials materials systems used various forms of carbon/carbon (C/C) for the substrate. The Starfire and RCI substrates were carbon fiber/ hafnium diboride (HfB_2) based matrix materials. The General Electric Power Systems (GEPS) and the Ultramet coated materials used the identical GEPS carbon fiber/silicon carbide (C/SiC) substrate.

Table 1. Material Systems Tested

	Substrate	**Coating**
General Atomics	BFG brake C/C	70wt% HfC/30wt% HfB_2
Engelhard	Hitco C/C	Ir/HfO_2
MER	MER C/C	CVD SiC/CVD HfC
Starfire	Pan X33, Preceramic HfB_2/SiC	Preceramic HfB_2/SiC
RCI	K321 4:1, HfB_2 based	HfC based
Synterials	CCAT C-C 1K-tow	Si_3N_4
GEPS	GEPS C/SiC	GEPS CVIP (SiC based)
Ultramet	GEPS C/SiC	Ultra 2000

All specimens except for the GEPS and Ultramet were nominally 0.25 inches thick and 2.8 inches diameter. The GEPS and Ultramet specimens were nominally 0.1 inches thick and 2.8 inches in diameter

TEST FACILITIES AND EQUIPMENT

The NASA JSC Atmospheric Reentry Materials and Structures Evaluation Facility was used to conduct the plasma arc convective heating tests. Test gases (77 percent nitrogen and 23 percent oxygen) were heated by a segmented constricted arc heater and expanded into a vacuum chamber through a water-cooled nozzle. For this test a conical nozzle with a 15-degree half angle, a 2.25-inch throat and an exit diameter of 5 inches was used. Test specimens were mounted on two water-cooled, remotely actuated sting arms that allowed them to be inserted after test conditions stabilized. A 4-inch diameter flat-face model configuration that accommodates a 2.8-inch diameter flat specimen was used. For most of the runs the insertion arm was 10.5 inches from the nozzle exit. The pressure test conditions were established using a 4-inch diameter flat face pressure model.

A scanning spectroradiometer was used to estimate temperatures and emissivities. Data was acquired at over 400 discrete wavelengths between 0.7 and 8 microns in 4 bands. The measurement angle was 57 degrees from the normal. The acquired data was fed into a computer program that identified the best fit for temperature and emissivity by iteration of Planck's function. A blackbody standard was used to certify the scanner. Limitations to the technique were that it is only applicable to gray-body emission radiators and that the temperature must be stable during the scan period without excessive temperature gradients across the view.

EMISSIVITY/TEMPERATURE MEASUREMENT TEST PROCEDURE

As-received weights of all test specimens were recorded. Specimens were then dried and weights recorded. Pictures of both front and back surfaces were taken before a specimen was exposed to the arc jet.

The arc jet test conditions used are shown in Table 2. The initial conditions were set at 3170 BTU/lb enthalpy (energy balance method), 108 psf impact pressure and a cold wall heating rate of 100 $BTU/ft^2 \cdot sec$. These conditions were picked because they gave a steady state temperature of 2600°F for Reinforced Carbon-Carbon (RCC) which was considered to be a good starting point. To get emissivity as a function of temperature, the arc jet was ignited and the initial conditions were brought to steady state. A specimen was inserted into the stream and after the surface temperature stabilized, a spectroradiometer measurement was taken. The arc jet power was increased to the next test condition with the specimen left in the stream. After the surface temperature stabilized at the new set of conditions, another spectroradiometer measurement was made. This sequence of steps was continued until the specimen failed. After failure, the sting was removed from the stream and the arc jet conditions were again set to condition number 1 and the second sting was inserted and the whole process was repeated. Each specimen was exposed to the same set of arc jet conditions up until its failure. The most severe conditions used were 5630 BTU/lb enthalpy (energy balance method), 230 psf impact pressure and a cold wall heating rate of 250 BTU/ft^2·sec. Emissivity and temperature values were calculated from the radiometer after completion of the run.

Table 2. Arc Jet Test Conditions

Condition Number	Current, Amps	Flow Rate, lb_m/sec	Power, MW	Enthalpy, BTU/lb_m	Impact Pressure, psf	Cold Wall Heating Rate, BTU/ft_2·sec	RCC Steady State Temperature, °F
1	400	0.20	0.97	3170	108	100	2600
2	500	0.25	1.31	3660	142	125	2830
3	550	0.30	1.56	3730	170	137	2970
4	650	0.30	1.82	4300	183	162	3150
5	750	0.30	2.08	4720	197	191	3210
6	850	0.32	2.43	5170	217	221	>3250
7	950	0.32	2.73	5630	230	250	N/A
8	1050	0.32	3.01	6150	239	283	N/A
9	1150	0.32	3.27	6460	247	307	N/A
10	1250	0.32	3.53	6900	250	330	N/A

A specimen was considered to have failed when the coating failed exposing the substrate surface. Coating failure could be caused by such phenomena as hot spot development, coating spallation, and coating ablation, all resulting in substrate surface exposure. Catastrophic breakup of specimen from thermal shock or thermal stress was another possible failure mode.

MASS LOSS and COATING DURABILITY TEST PROCEDURE

As-received weights and thickness measurements of all test specimens were made and recorded. Specimens were dried and the weight recorded. Pictures of both front and back surfaces were taken before exposure to the arc jet. Test condition number 5 shown in Table 2 was the arc jet test condition used for the phase 2 (cyclic durability) and phase 3 (one-hour duration) testing. This condition was chosen since it was the most severe condition that all material systems survived during the phase 1 testing.

For the cyclic durability tests, the goal was to expose each material system specimen to 10, 10-minute cycles. The test procedure planned to accomplish this was as follows. Specimens were to be installed in both stings. The arc jet would be brought to steady state conditions for the test point and one of the specimens was to be inserted into the flow for 10 minutes. After 10 minutes the specimens was to be removed from the flow and the 2nd specimen was to be inserted into the flow. After 10 minutes the 2nd specimen was to be removed from the flow and the first specimen was to be inserted back into the flow. This switching of specimens was to be continued until each specimen had been exposed to 5 cycles. After 5 cycles, the specimens were to be removed and weights and thickness measurements were to be taken. The specimens were to be reinstalled and exposed for an additional 5, 10-minute cycles. After exposure, weight, thickness measurements were to be made and pictures of both the front and back surfaces were to be taken. During each 10-minute cycle, 2 emissivity measurements were to be made. As explained in the Phase 2 results section, some specimens were also weighted after 3, 10-minute cycles and after 7, 10-minute cycles.

The test procedure planned for the one-hour duration test was as follows. The arc jet would be brought to steady state conditions for the test point and a specimen would then be inserted into the flow for 60 minutes. During the exposure, emissivity measurements were to be taken every 500 seconds. After 60 minutes the specimen would be removed from the flow. If the coating were to fail before 60 minutes had elapsed, the specimen would be removed from the flow. After exposure, weight and thickness measurements were to be made and pictures of both the front and back surfaces were to be taken. This procedure was followed for the only specimen tested in phase 3.

PHASE 1 RESULTS

The emissivity verses temperature plot for two General Atomic hafnium carbide/hafnium diboride (HfC/HfB_2) coated material specimens are shown in Figure1. The numbers on the chart indicate the arc jet test condition. The two specimens had similar behavior. Both failed after test condition 7. Failure was attributed to coating spallation. The emissivity values were extremely low, resulting in surface temperatures of over 4000°F for all tested conditions. The emissivity increased as the test progressed, ranging from 0.16 initially to 0.49 just before failure. These low emissivity values led to surface temperature increases of about 1200°F compared to RCC at identical arc jet conditions.

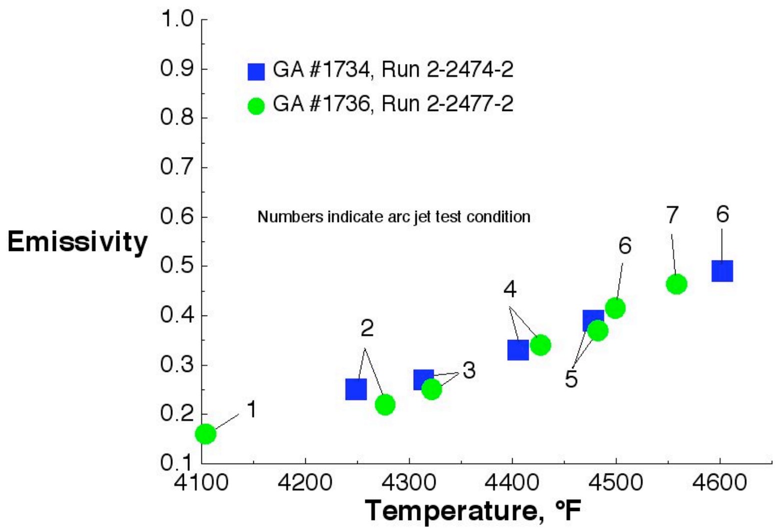

Figure 1. Emissivity versus temperature for GA 70 wt% HfC 30 wt% HfB_2 coated material.

The emissivity verses temperature plot for the Engelhard iridium/hafnium oxide ($Ir/Hf0_2$) coated material is shown in Figure 2. Only one specimen was available for testing. The material failed due to coating spallation after condition 7. The plot is similar to that of the General Atomics material .The emissivity values started out low and increased as the test progressed. The emissivity values are higher than that for the General Atomics material but still relatively low, ranged from 0.38 to 0.58. The low emissivity values led to surface temperatures ranging from 3700°F to over 4500°F, again much higher than for RCC at identical arc jet conditions.

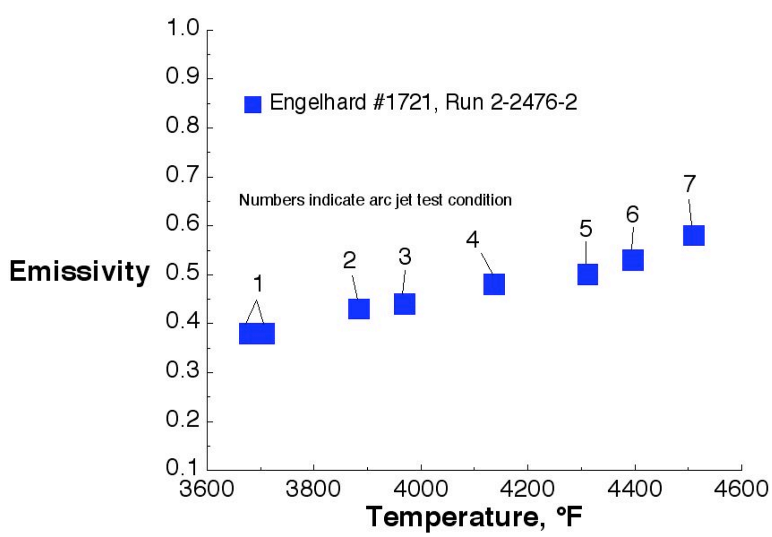

Figure 2. Emissivity versus temperature for Engelhard $IrHfO_2$ coated material.

The emissivity verses temperature plots for two MER silicon carbide/hafnium carbide (SiC/HfC) coated material specimens are shown in Figure 3. The trends of both specimens were similar. One specimen failed after test condition 4 and the other failed after test condition 5. Both failed due to hot spot development at around 3250°F. The initial emissivity was about 0.83 and increased to about 0.95 and then decreased to about 0.80. Temperatures ranged from 2600°F to about 3250°F at failure.

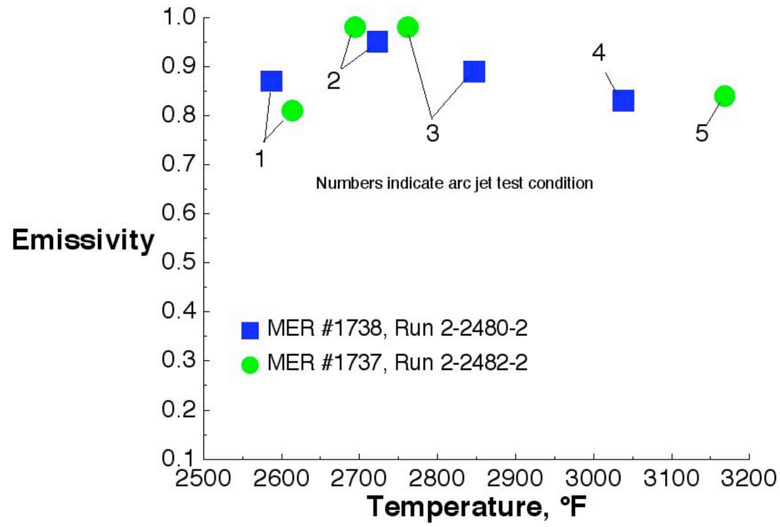

Figure 3. Emissivity versus temperature for MER SiC/HfC coated materials.

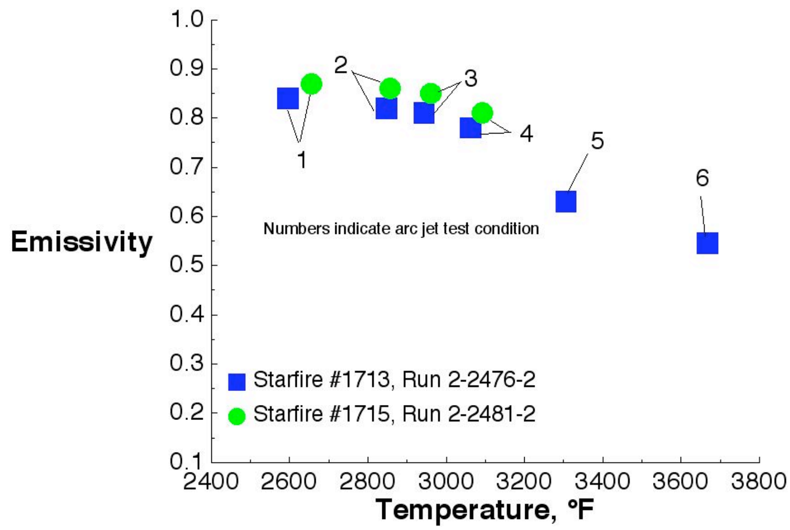

Figure 4. Emissivity versus temperature for Starfire preceramic SiC/HfB_2 coated materials.

The emissivity verses temperature plot for the Starfire Preceramic HfB_2/SiC coated material is shown in Figure 4. Two specimens were run and the trends of both specimens were consistent with each other. One specimen failed after test condition 4 and the other failed after test condition 6. Both failed due to hot spot development. The initial emissivity was about 0.86 and held pretty constant through the first 4 test conditions and then dropped off to 0.55. One specimen failed at around 3250°F but the 2nd specimen survived past 3650°F which indicates a potential for use above 3250°F.

Eight specimens were received from Starfire. Four were made in one batch and four were made in a second batch. The specimens mentioned above both came from the same first batch. Two specimens from the second batch were also tested and both suffered catastrophic failure from thermal shock or thermal stress buildup after about 10 seconds of exposure to test condition 1. In analyzing the production runs of the two batches, it was found that there were significant differences in the matrix composition. The results point out the need for stringent quality control in composite fabrication.

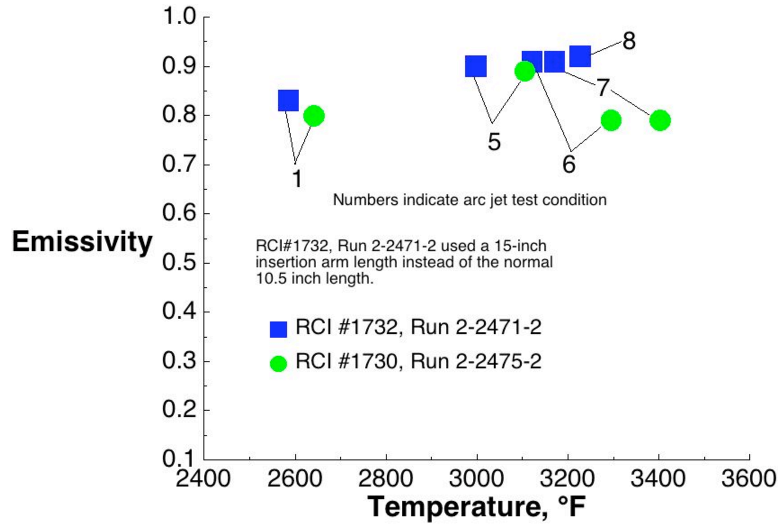

Figure 5. Emissivity versus temperature for RCI HfC-based coated materials.

The emissivity verses temperature plot for two RCI HfC-based coated material specimens are shown in Figure 5. Specimen #1732 was the first specimen run in this test series and the insertion arm was set 15 inches from the nozzle exit for the test. The specimen did not fail at this insertion arm distance after being exposed to test condition 8 so the test was stopped and the insertion arm was moved up to be only 10.5 inches from the nozzle exit. All subsequent runs in this test program were run with the insertion arm set to 10.5 inches from the nozzle exit. The 2nd RCI specimen failed after test condition 7 using the new shorter insertion arm distance. Specimen #1732 was run a second time at the new sting location and failed after test condition 6. The emissivity data for the second run of specimen #1732 is not plotted. Both specimens failed due to hot spot development. Specimen #1732 failed at around 3250°F but the 2nd specimen survived beyond 3400°F, again indicating a potential use above 3250°F. The emissivity trend of both specimens was again consistent. The initial emissivity was about 0.80. One unique feature about the RCI material was that for both specimens, emissivity calculations could not be made for test conditions 2 through 4. It is possible that the chemical reactions going on between 2600°F and 3000°F make the surface behave as a non-gray radiator. For the 2nd RCI specimen the emissivity dropped from 0.9 to 0.8 above 3200°F.

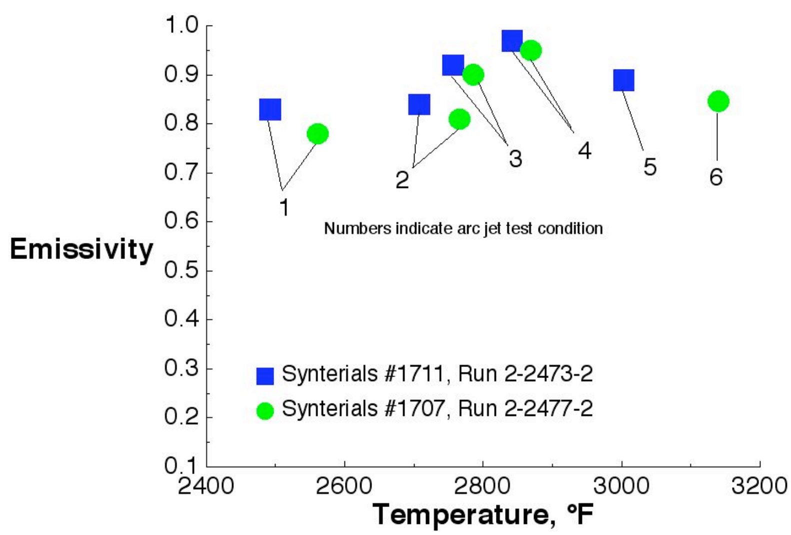

Figure 6. Emissivity versus temperature for Synterials Si_3N_4 coated materials.

The emissivity verses temperature plot for the Synterials silicon nitride (Si_3N_4) coated material is shown in Figure 6. Two specimens were tested and the trends of both specimens were consistent. One specimen failed after test condition 5 and the other failed after test condition 6. Both failed due to hot spot development at around 3250°F. The initial emissivity was about 0.83, subsequently increased to about 0.95 and then decreased to about 0.85. Temperatures ranged from 2500°F to about 3250°F at failure. The data was similar to the MER data.

The emissivity verses temperature plot for the Ultramet Ultra 2000 coated material is shown in Figure 7. Due to time constraints, only one specimen was run. The specimen failed after test condition 7 at temperatures slightly above 3250°F due to hot spot development. The initial emissivity was 0.84, subsequently increased to 0.88 at 2625°F and then gradually decreased to 0.80 at 3200°F.

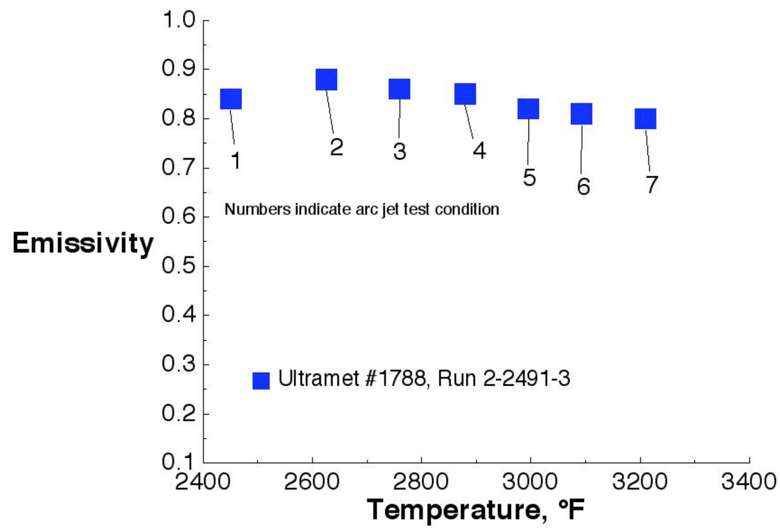

Figure 7. Emissivity versus temperature for Ultramet Ultra 2000 coated materials.

PHASE 2 RESULTS

The purpose of this phase was to determine if the material systems had any thermal cycling durability. Engelhard and MER material were not tested in this phase due to the shortage of material. GA, Synterials, and Starfire specimens all failed during the first cycle due to hot spot development. An RCI specimen completed all 10 cycles. A GEPS specimen completed 7 cycles and an Ultramet specimen completed 5 cycles before testing time ran out. Neither the GEPS or Ultramet specimen had failed at the time the testing was stopped.

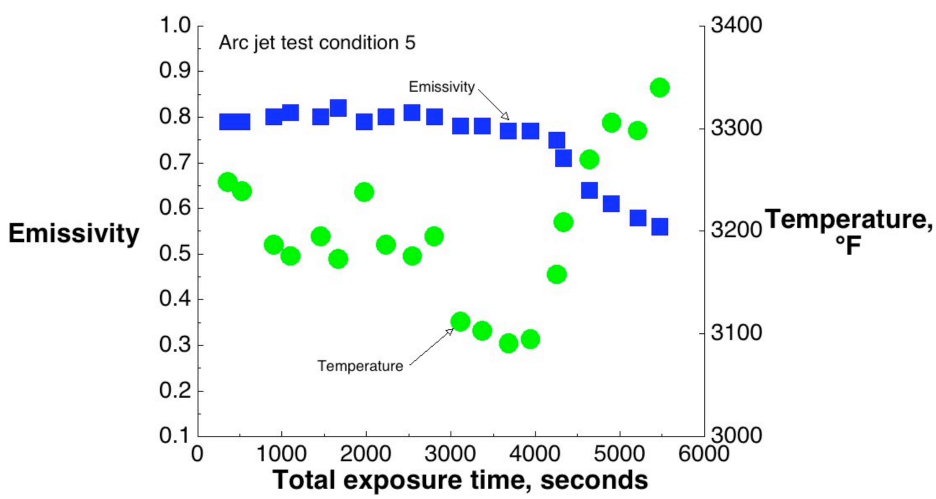

Figure 8. Emissivity as a function of cyclic exposure time for the RCI HfC-based coated material

As mentioned in the procedure section, specimens were to be weighed after 5 and 10 cycles. The RCI specimen was also weighed after 3 cycles since the initial run had to be terminated after 3 cycles were completed. The RCI specimen lost 1.30 percent of its weight after 3 cycles, 3.28 percent after 5 cycles and lost 10.33 percent of its weight after 10 cycles. Emissivity measurements were taken twice during each 10-minute cycle. The emissivity data is shown in Figure 8. The emissivity was fairly constant at about 0.80 for the first 5 cycles and then started to drop off rather sharply during the last 3 cycles reaching 0.56 after 10 cycles.

The GEPS specimen was weighed after 3 cycles in order to get a comparison with the RCI specimen and again after 7 cycles. The specimen lost 0.11 percent after 3 cycles and 1.74 percent after 7 cycles. Emissivity as a function of cycle time was also measured. The emissivity was pretty constant ranging from 0.82 to 0.85 for all 7 cycles.

The Ultramet specimen was weighed after 5 cycles. It lost 0.22 percent of its weight. The initial emissivity was measured to be 0.87 and it gradually dropped to 0.82 during the 5th cycle.

PHASE 3 RESULTS

The purpose of this third phase was to determine whether any of the materials that survived phase 2 testing could also survive an arc jet test of one-hour duration. Only the RCI material was tested in this phase. The GEPS and Ultramet materials were not tested due to lack of specimens and test time. Only one RCI specimen was exposed since only one specimen was available. It lost 1.12 percent of its weight. This weight loss was much less than the weight loss of the thermally cycled specimen. Emissivity measurements were taken every 500 seconds during the run. The plot of emissivity versus time is shown in Figure 9. The range of emissivity values from 0.79 to 0.85 is consistent with other RCI specimen values. A trend of increasing emissivity values as a function of time is seen in the data.

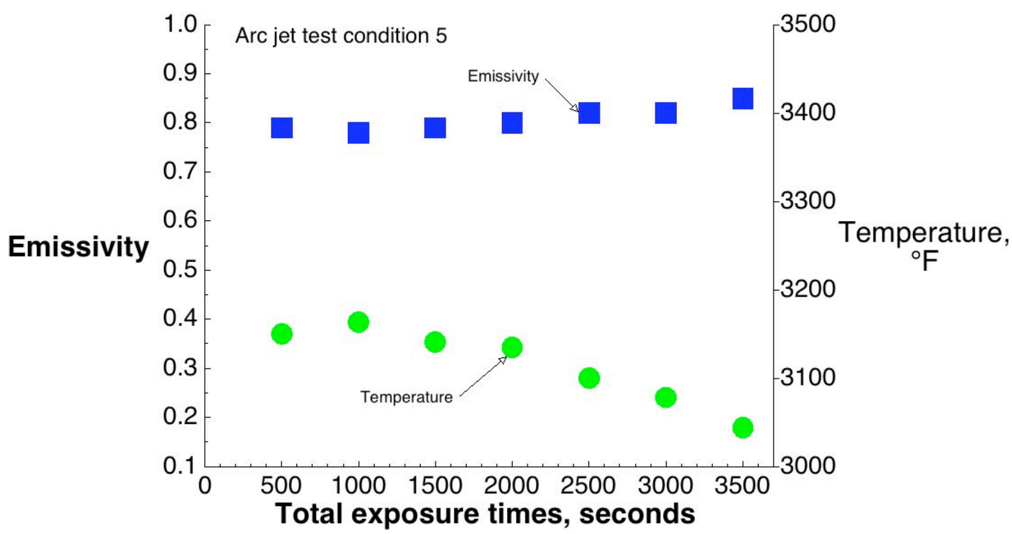

Figure 9. Emissivity as a function of cyclic exposure time for the RCI HfC-based coated material

DISCUSSION OF RESULTS

HfC/HfB_2 and Ir/$Hf0_2$ coatings had calculated emissivities in the range of 0.25 to 0.58, leading to surface temperature increases of about 1200°F compared to RCC at identical arc jet conditions. These low emissivity values make hafnium carbide/hafnium diboride and Iridium/Hafnium Oxide coatings systems unlikely candidates for leading edge applications.

Most coating systems failed due to the development of a hot spot that is thought to be the onset of active oxidation. For the Synterials and MER material this occurred at the arc jet conditions of 5170 BTU/lb enthalpy (under the energy balance method), 217 psf impact pressure and a cold wall heating rate of 221

BTU/ft^2·sec. The RCI and Ultramet material systems which both had HfC -based coating systems survived beyond a more severe arc jet condition of 6150 BTU/lb enthalpy, 239 psf impact pressure and a cold wall heating rate of 283 BTU/ft^2·sec before the onset of active oxidation, indicating that the HfC -based coating could possibly be used at higher heating rates than single phase silica-based coating systems before onset of active oxidation.

During the cyclic durability phase of the testing, the GA, Synterials, and Starfire specimens all failed during the first cycle using test condition 5, 4720 BTU/lb enthalpy, 197 psf impact pressure and a cold wall heating rate of 191 BTU/ft^2·sec. During phase 1, the materials survived test condition 5 but were only at the condition long enough for the temperature to stabilize for an emissivity measurement. During the phase 1, the materials failed at condition 6 so it was not too surprising that the materials failed at condition 5 during the phase 2.

An RCI specimen survived all 10 cycles. It failed phase 1 when the specimen was exposed to test condition 8, so it was not surprising that it lasted for all 10 cycles at test condition 5. The RCI specimen lost significant weight during the cycling. Since as-received mechanical properties were not known for the material and a residual strength test was not conducted, the correlation between weight loss and reduction in strength cannot be made. Like the RCI material, the Ultramet material failed phase 1 when the specimen was exposed to test condition 8 so again it was not surprising that it also survived multiple cycles at the test condition 5. It was exposed for 5 cycles. Additional cycles were not run since testing time elapsed. The GEPS material was not tested in phase 1 so there was no previous information to indicate how it would perform during phase 2. The GEPS specimen was exposed for 7 cycles. Additional cycles were not run since testing time elapsed. The weight losses seen in the specimens that were tested for cyclic durability indicate that lifetime use of these particular coating systems is probably limited to only a few missions when the coating are exposed to maximum temperatures of 3200°F.

As mentioned earlier, only the RCI material was tested in the phase 3. The specimen lost 1.12 percent of its weight after the one-hour exposure. This weight loss was much less than the weight loss of the thermally cycled specimen, thus indicating that thermal cycling has a much more detrimental effect on oxidation performance than constant temperature testing. This is not surprising since thermal stresses arising from CTE mismatches and phase changes during heating and cooling operations are detrimental to coating adhesion.

Some abort profiles being investigated require the leading edges to sustain high heat loads for extended times. The fact that the RCI material survived and had low mass loss after a one-hour exposure indicates that there is potential for leading edge materials to survive this type of abort profile.

Emissivity measurements were made during all three phases of the test program. This was done in order to get an idea of emissivity value variability between specimens and to see what changes if any would occur in emissivity due to thermal cycling or long term constant exposure.

The Ultramet material was tested in both phases 1 and 2. During phase 1, the initial emissivity was 0.84, increased to 0.88 and then trailed off to end at 0.80. Under phase 2 testing, the initial value during the first cycle was 0.87. The 2nd reading of the first cycle was 0.84. For cycle 2 and 3, the emissivity was 0.83 and for the 4th and 5th cycles, the emissivity was 0.82. The range of values was similar for both specimens and at least for 5 cycles the emissivity of the Ultramet material was pretty constant.

The RCI material was tested in all three phases of the test program. Results from the phase 1 test shown in Figure 5, showed emissivity values of 0.83 to 0.92 for one specimen and 0.79 to 0.89 for a second specimen. During the phase 2 testing, as shown in Figure 8, the emissivity was fairly constant for the first 7 cycles in the range of 0.77 to 0.82 and then rapidly dropped off during cycles 8 through 10. No emissivity value close to 0,90 was measured during any cycle. It is not known why the emissivity values were lower but it could be due to material variability or the fact that the coating surface chemistry might well be different due to the different arc jet test conditions. As shown by Figure 9, during the third phase the emissivity dipped slightly from 500 to 1000 seconds but then increased for the rest of the run. Emissivity ranged from 0.79 at 500 seconds to 0.85 at 3500 seconds.

Due to the limited data set, no definite conclusions can be made regarding how emissivity changes with time both in steady state test conditions and thermal cycling environments but the data gives some insight into the effects of thermal cycling and time on emissivity for the Ultramet and RCI coating systems.

SUMMARY AND CONCLUSIONS

HfC/HfB_2 and $Ir/Hf0_2$ coatings had calculated emissivities in the range of 0.25 to 0.58 leading to surface temperature increases of about 1200°F compared to RCC at identical arc jet conditions. These low emissivity values make Hafnium Carbide/Hafnium Diboride and Iridium/Hafnium Oxide coatings systems unlikely candidates for leading edge applications.

Estimated emissivities of other coatings systems evaluated started at around 0.85, tended to increase to 0.9 or higher and then dropped off leading to temperatures slightly lower than RCC at identical arc jet conditions.

Except for the HfC/HfB_2 and $Ir/Hf0_2$ coatings, all other coating systems failed due to the development of a hot spot which is due to the onset of active oxidation The onset of active oxidation for the HfC -based coating systems occurred at higher heating rates than single phase silica-based coating systems, indicating that they might be more suitable for certain mission environments.

During the cyclic durability phase of the testing, only three materials survived past the first cycle. The weight lost seen in the specimens that were tested for cyclic durability indicate that lifetime use of these particular coating systems is limited only a few missions when the coatings are exposed to maximum temperatures of 3200°F.

The weight loss of the RCI specimen that was subjected to a continuous one-hour exposure was much less than the weight loss of the specimen that was thermally cycled indicating that thermal cycling has a much more detrimental effect on oxidation performance than constant temperature testing. Some abort profiles being investigated require the leading edges to sustain high heat loads for extended times. The fact that the RCI material survived and had low mass loss after a continuous one-hour exposure indicate that there is potential for leading edge materials to survive this type of abort profile.

Emissivity values comparisons between test phases were made only with the Ultramet and RCI materials since these were the only materials where emissivity data were generated for more than one test phase. Due to the limited data set, no definite conclusions could be made regarding how emissivity changes with time both in steady state test conditions and thermal cycling environments, but the data gives some insight into the effects of thermal cycling and time on emissivity for the Ultramet and RCI coating systems.

The results of this study indicate that for mission environments that have maximum temperatures around 3200°F, oxidation protections improvements are needed to get more than low single digit mission lifetime reusability.