

**Emissivity Results On High Temperature Coatings for Refractory Composite
Materials**

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ABSTRACT

The directional emissivity of various refractory composite materials considered for application for reentry and hypersonic vehicles was investigated. The directional emissivity was measured at elevated temperatures of up to 3400°F using a directional spectral radiometric technique during arc-jet test runs. A laboratory-based relative total radiance method was also used to measure total normal emissivity of some of the refractory composite materials. The data from the two techniques are compared. The paper will also compare the historical database of Reinforced Carbon-Carbon emissivity measurements with emissivity values generated recently on the material using the two techniques described in the paper.

INTRODUCTION

Emissivity is an important parameter needed for thermal protection systems (TPS) used on hypersonic and reentry vehicles. The TPS typically consists of insulative systems such as ceramic tiles that can withstand temperatures as high as 2300°F or hot structures made from oxidation-resistant carbon-carbon (C-C) or ceramic matrix composites (CMC) that can withstand higher temperatures, typically up to 3200°F. For either system a high value of emissivity is desirable. The high convective heating rates associated with hypersonic flight are balanced by radiation heat transfer from the surface to deep space and also by conduction heat transfer into the TPS and the underlying structure. Typical TPS design requires a high surface emissivity value so that most of the impinging convective heating is

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radiated out, resulting in a lower amount of heat being conducted into the underlying structure

During NASA's Next Generation Launch Technology (NGLT) Program and other follow-on research programs, many materials were tested in an arc jet, and during these tests, directional emissivity measurements were made. This paper will present the emissivity values measured for some of these materials.

There is much of interest in the possible use of carbon fiber reinforced silicon carbide composite materials for hot structures and thermal protection systems [1, 2]. Emissivity measurements made on C/SiC during the NGLT program will be compared to more recent measurements.

RCC emissivity values were generated during the NGLT program and follow-on research activities and these values will be compared to historical measurements.

EMISSIVITY MEASUREMENT

Emissivity of any surface is a function of wavelength, direction, temperature, and surface conditions. Surface conditions include factors such as roughness, oxide layers, contamination, grain structure, etc. The emissivity data required for TPS design is the total (integrated over wavelengths) hemispherical (integrated over all directions above the surface) emissivity as function of temperature. Typical measurements are made either on a total or spectral basis, with the spectral data being integrated over all measured wavelengths to obtain total properties. Obtaining total hemispherical emissivity at high temperatures is difficult. Typically only directional data at specific viewing angles (normal, near normal or at an angle between 45 and 60 degrees) is generated at high temperatures. The calculation of hemispherical emissivity from the directional emissivity is an approximation. Usually, the ratio of measured hemispherical to directional emissivity at room temperature is assumed to be applicable at higher temperatures [3]. Therefore, the directional total emissivities measured at elevated temperatures are multiplied by the room-temperature ratio of hemispherical to directional emissivity. The two techniques used for measuring directional total/spectral emissivity used in this study are briefly described.

Southern Research Institute Relative Total Normal Radiance Technique

Total normal emissivity is measured by comparing the energy received by a thermopile from a sample to that received from a blackbody cavity at the same temperature. The total amount of thermal energy for all wavelengths emitted by a blackbody is:

$$I_B = \int_{\lambda=0}^{\lambda=\infty} I_{\lambda} d\lambda \quad (1)$$

where I_{λ} is the spectral intensity and λ the wavelength. The amount of thermal radiation for all wavelengths emitted by a non-blackbody emitter is:

$$I_s = \int_{\lambda=0}^{\lambda=\infty} \varepsilon_{\lambda} I_{\lambda} d\lambda \quad (2)$$

The total normal emissivity can be defined by integrating and combining equations (1) and (2):

$$\varepsilon_n = \frac{I_s}{I_B} \quad (3)$$

Therefore, if a sensitive receiver of the thermal energy spectrum, such as a thermopile, is used for measurement of radiation, and if it has characteristics so as to give a response of voltage, V , which is proportional to the magnitude of the radiant energy received per unit time, W , then the total normal emissivity of a specimen material can be obtained. The required condition is that the ratio of the specimen voltage (V_s) and the blackbody voltage (V_B) indicated by the thermopile normal to a thermal emitter at a known temperature, be determined experimentally. The specimen emissivity can then be written as the ratio of the radiant energy received per unit time and/or as the ratio of the respective voltages:

$$\varepsilon_n = \frac{W_s}{W_B} = \frac{V_s}{V_B} \quad (4)$$

The apparatus used by Southern Research Institute to measure total normal emissivity from 1500°F (815°C) to 5000°F (2760°C) is shown in Figure 1. The specimen is supported in the center of the flat concentrator induction coil by a zirconia cylinder filled with fine zirconia grog. The radiometer views the specimen from directly above through a water-cooled tube. A water-cooled optical valve is used to blank off the specimen from the radiometer. Optical-temperature readings are taken through the main port, which may be pushed in to view the specimen through a mirror from directly above. Viewing ports contain sapphire windows. The portion of the furnace above the specimen is water-cooled to eliminate energy being reflected back onto the specimen surface. The emissivity furnace is built of steel and sealed with "O" rings so that a vacuum may be attained. The voltage generated by the receiver is measured with a microprocessor based voltmeter. Temperatures are measured with an optical pyrometer.

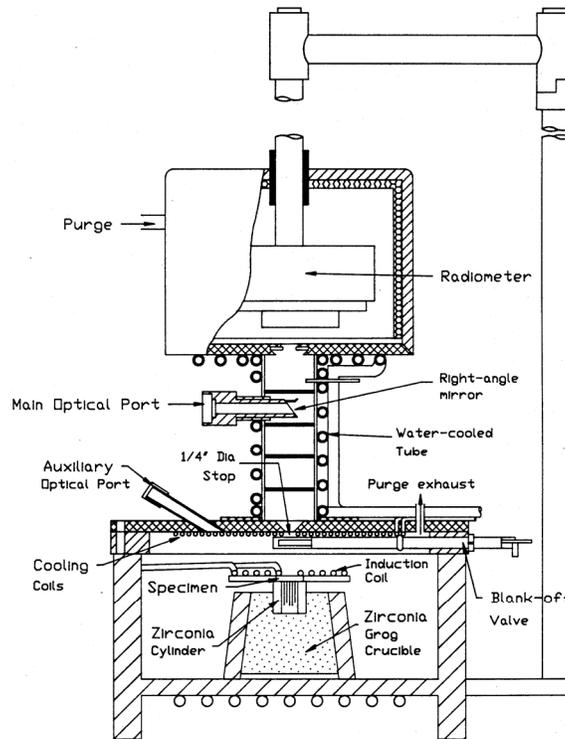


Figure 1. Relative Total Radiance Emissivity Facility

NASA Johnson Space Center Directional Spectro-radiometric Technique

The NASA Johnson Space Center (JSC) Atmospheric Reentry Materials and Structures Evaluation Facility [4] uses a scanning spectro-radiometer 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 normal so the data collected is directional emissivity. 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. The technique is only applicable to gray-body emission radiators and requires temperature to be stable during the scan period without excessive temperature gradients across the view.

RESULTS AND DISCUSSION

NASA's Next Generation Launch Technology Program

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 [5] on thirteen material systems which were evaluated for possible use on the nose leading edge of the X-43A Mach 10 vehicle [6]. Six material systems survived three, 130-second cycles. During this time frame, NASA's Next Generation Launch

technology Program (NGLT) was trying to develop passive refractory composite leading edge materials that would have multiple reuse capability at temperatures up to 3600°F. The material systems that survived the AEDC tests were evaluated for use in this program. An expanded arc-jet test program was conducted at the NASA JSC Atmospheric Reentry Materials and Structures Evaluation Facility. 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 whether the material systems had any thermal cycling durability and to see whether emissivity values would change during this thermal cycling. The purpose of the third phase was to determine whether the materials could survive an arc jet test of one-hour duration and to see whether emissivity values would change during the one-hour exposure. Phase one results will be discussed in this paper. Phase 2 and 3 results and a more detailed discussion of the test are reported in reference [1].

TEST MATERIALS

The material systems tested are listed in Table 1. 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 (HfB₂) 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

Manufacturer	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, Pre ceramic HfB ₂ /SiC	Pre ceramic HfB ₂ /SiC
RCI	K321 4:1, HfB ₂ based	HfC based
Synterials	CCAT C-C 1K-tow	Si ₃ N ₄
GEPS	GEPS C/SiC	GEPS CVIP (SiC based)
Ultramet	GEPS C/SiC	Ultra 2000

TEST CONDITIONS

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/ft².sec. These conditions were chosen because they gave a steady state temperature of 2600°F for reinforced carbon-carbon (RCC) which was considered to be a good starting point. 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/ft².sec.

Table 2. Arc-Jet Test Conditions

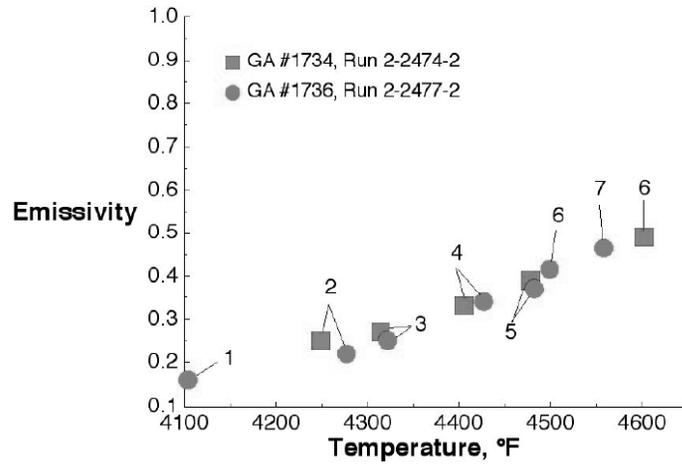
Condition Number	Current, Amps	Flow Rate, lb _m /sec	Power, MW	Enthalpy, BTU/lb _m	Impact Pressure, psf	Cold Wall Heating Rate, BTU/ft ² .sec	RCC Steady State Temperature, °F
1	400	0.20	0.97	3170	108	100	2600
2	500	0.25	1.31	3660	142	125	2830
3	550	0.30	1.56	3730	170	137	2970
4	650	0.30	1.82	4300	183	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

PHASE 1 RESULTS AND DISCUSSION

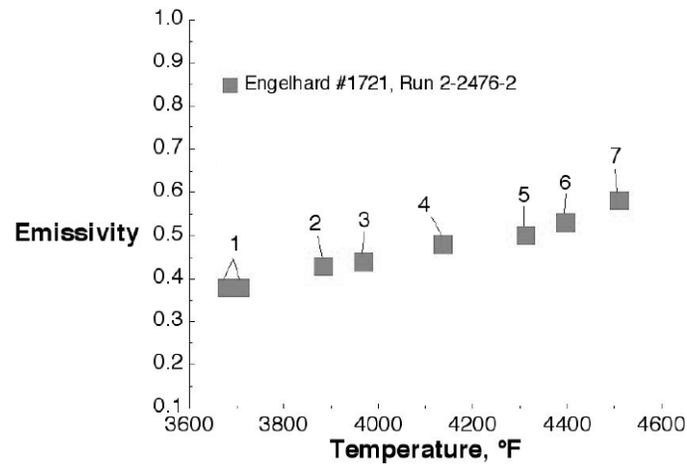
The emissivity versus temperature plot for two General Atomic hafnium carbide/hafnium diboride (HfC/HfB₂) coated material specimens are shown in Figure 2a. The numbers on the chart indicate the arc-jet test condition. The two specimens had similar behavior. Both failed after test condition 7. Failure 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.

The emissivity versus temperature plot for the Engelhard iridium/hafnium oxide (Ir/HfO₂) coated material is shown in Figure 2b. Only one specimen was available for testing. The material failed due to coating spallation after condition 7. The plot is similar to that for 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, ranging 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.

The emissivity versus temperature plots for two MER silicon carbide/hafnium carbide (SiC/HfC) coated material specimens are shown in Figure 3a. 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.

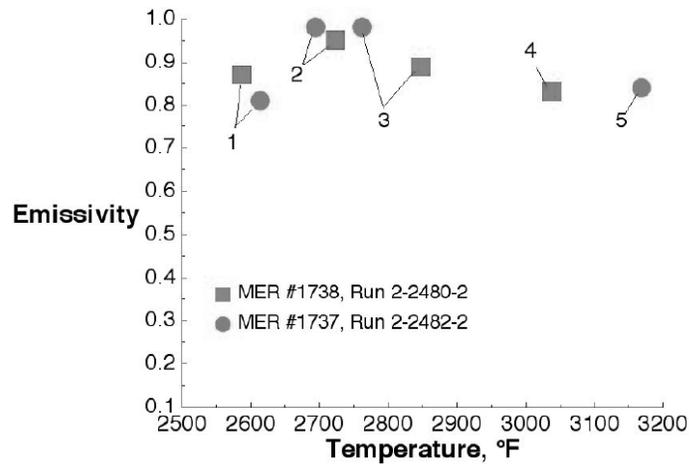


2a)

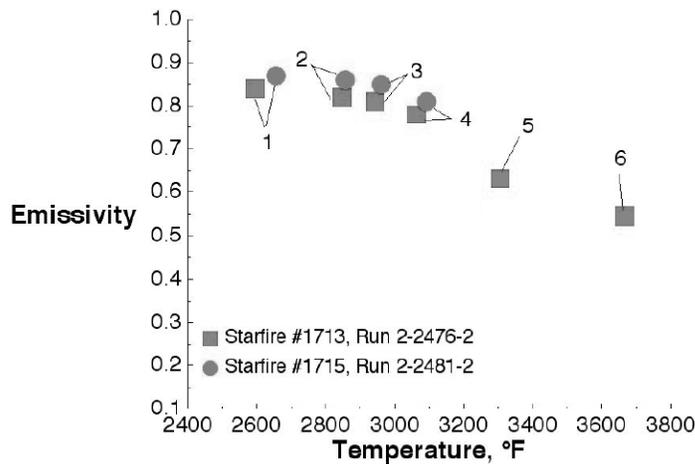


2b)

Figure 2. Emissivity versus temperature for a) GA 70 wt% HfC 30 wt% HfB₂ coated material, b) Engelhard IrHfO₂ coated material. (Numbers indicate arc jet test conditions)



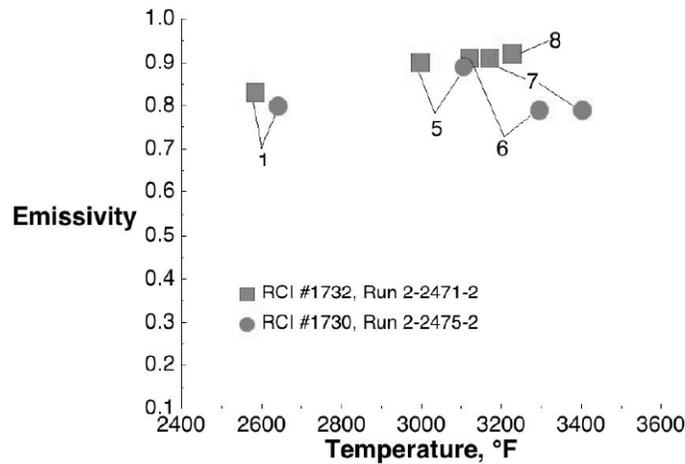
3a)



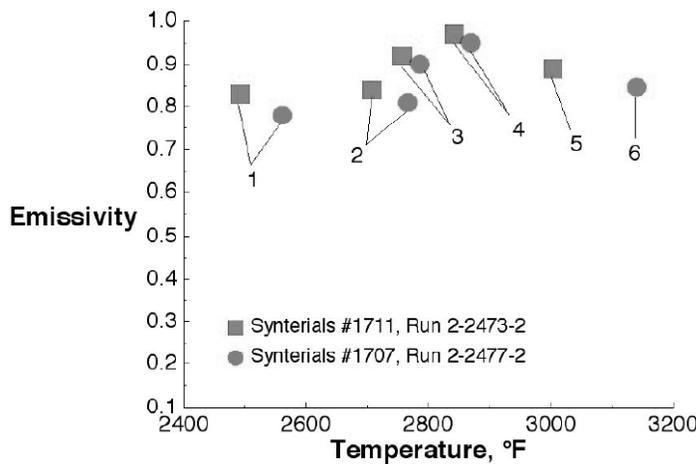
3b)

Figure 3. Emissivity versus temperature for a) MER SiC/HfC coated materials, b) Starfire preceramic SiC/HfB₂ coated materials. (Numbers indicate arc jet test conditions)

The emissivity versus temperature plot for the Starfire Preceramic HfB₂/SiC coated material is shown in Figure 3b. 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 mostly 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, suggesting potential for use above 3250°F



4a)



4b)

Figure 4. Emissivity versus temperature for a) RCI HfC-based coated materials, b) Si₃N₄ coated materials. (Numbers indicate arc jet test conditions)

The emissivity versus temperature plot for two RCI HfC-based coated material specimens is shown in Figure 4a. 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 second 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 second specimen survived beyond 3400°F, again indicating potential for 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.

The emissivity versus temperature plot for the Synterials silicon nitride (Si_3N_4) coated material is shown in Figure 4b. 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 versus temperature plot for the Ultramet Ultra 2000 coated material is shown in Figure 5. 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.

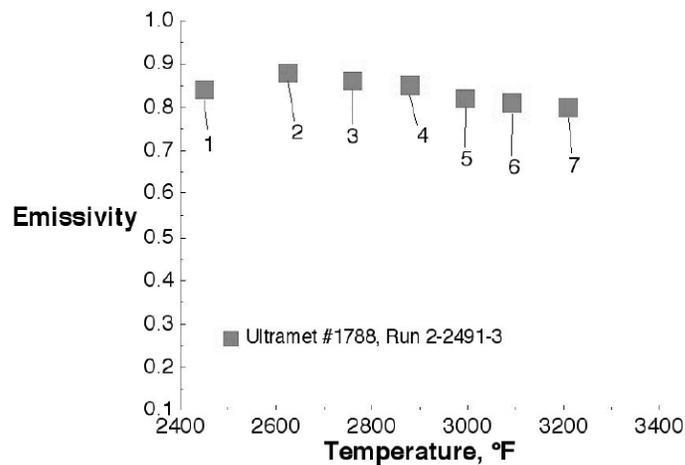


Figure 5. Emissivity versus temperature for Ultramet Ultra 2000 coated materials. (Numbers indicate arc jet test conditions)

Silicon Carbide Emittance Data Comparison

Coated carbon/silicon carbide (C/SiC) composite material (see Table 1) was tested during phase 2 of the NGLT test program. The coating on this specimen was a silica based coating designated as CVIP by the vendor. The specimen was subjected to test condition 5 (Table 2) in the JSC arc jet for seven 10-minute cycles. Emissivity measurements were taken twice during each cycle. The emissivity values (total directional) are shown in Figure 6, plotted as triangles. The values are clustered between 0.82 and 0.85 and thus did not change significantly with thermal cycling. Emissivity measurements (total directional) as a function of temperature measured in the JSC arc jet on C/SiC composite material coated with an oxidation-

protection coating designated as MCM-700 by the vendor during a more recent research program are also shown in Figure 6. The values are shown as squares. Emissivity values were generated at six pre-set test conditions listed in Table 3. The final test condition which generated the final 3270°F datapoint is not listed.

Table 3. 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	0.50		5330	74	56	2200
2	600	0.50		7460	85	84	2500
3	650	0.60		7414	101	91	2600
4	730	0.60		8070	105	101	2700
5	810	0.65		8327	117	110	2800
6	970	0.65		9663	127	133	2960

From 2400°F to 2740°F, the emissivity dropped from 0.84 to 0.72. From 2740°F to 2934°F, the emissivity rose to 0.74. At 3271°F, the emissivity dropped to 0.69. The data indicate that the two coatings have significant differences in emissivity. This was not totally unexpected, since the coating systems have different chemistries. The trend of decreasing emissivity as temperature increases shown by the MCM-700 coating is similar to that shown in Figures 3 through 5 for other coating systems.

SRI has also measured the emissivity (total normal) of uncoated C/SiC recently and the values they measured are plotted (circles) in Figure 6. The values increase with temperature. At 1678°F, the emissivity is 0.92 and rises to 0.99 at 3199°F.

The uncoated C/SiC has higher emissivity than either of the coated C/SiC materials. The reason is unclear. It could be due to chemistry differences between the uncoated surface and the two coating. The fact that a different technique was used to measure the emissivity of the uncoated specimens than used for the coated specimens and the additional fact that the uncoated values are total normal data while the coated values are total directional, might also play a role in the difference.

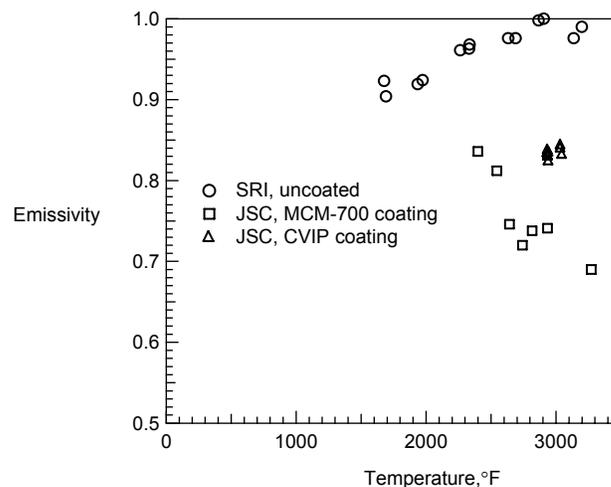


Figure 6. Variation of C-SiC emissivity with temperature

RCC Emissivity Data Comparison

The total directional emissivity of RCC at 57 degrees from normal, measured using the spectro-radiometer technique during the NGLT arc-jet testing program at NASA JSC is shown (circles) in Figure 7. The RCC specimen was used during the arc jet tests to establish the flow conditions required for testing of the samples studied in this test program. The normal emissivity of RCC was also measured recently by SRI using their relative total radiance technique, and the data are shown in the figure. The SRI data indicate normal emissivity of 0.97 and 0.99 between 1800 and 3000°F, while the JSC arcjet directional emissivity data are between 0.88 and 0.91 between 2700 and 3000°F. The normal total emissivity data used for Shuttle design [7] are also provided. The design data show a significant decrease in normal emissivity above 2000°F, with emissivity dropping from 0.89 at 2000°F to 0.54 at 3040°F. Even though the JSC arc-jet data are closer to the design data, they do not indicate a decrease in emissivity with increasing temperatures. The most recently published measured normal total emissivity data on virgin and flown RCC samples in the literature [3] are also shown in the figure. The data from Ref [3] more closely match the design RCC data than the data generated in the present study using the two different techniques employed.

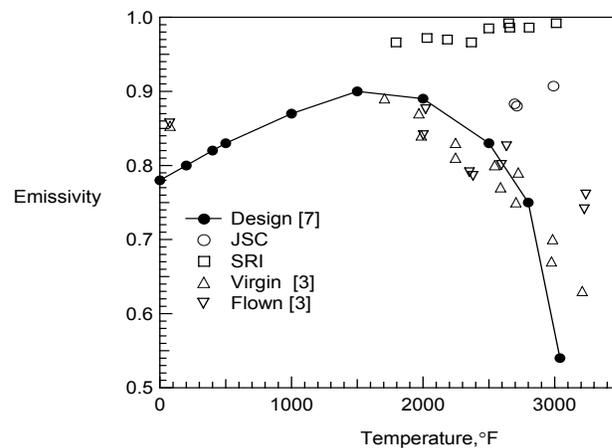


Figure 7. Variation of normal total emissivity of RCC with temperatures (JSC arc jet data at 57 deg from normal)

Non-Oxide Adhesive eXperiment (NOAX) Emittance Data For RCC Crack Repair

Non-Oxide Adhesive eXperimental (NOAX) is a paste-like material chosen for use for the on-orbit repair of crack and spallation damage to RCC. NOAX emissivity values are shown in Figure 8. The test articles consisted of RCC with the SiC coating removed and repaired in a thermal vacuum environment with NOAX to restore the damaged surface and inhibit oxidation of the underlying carbon substrate during reentry.

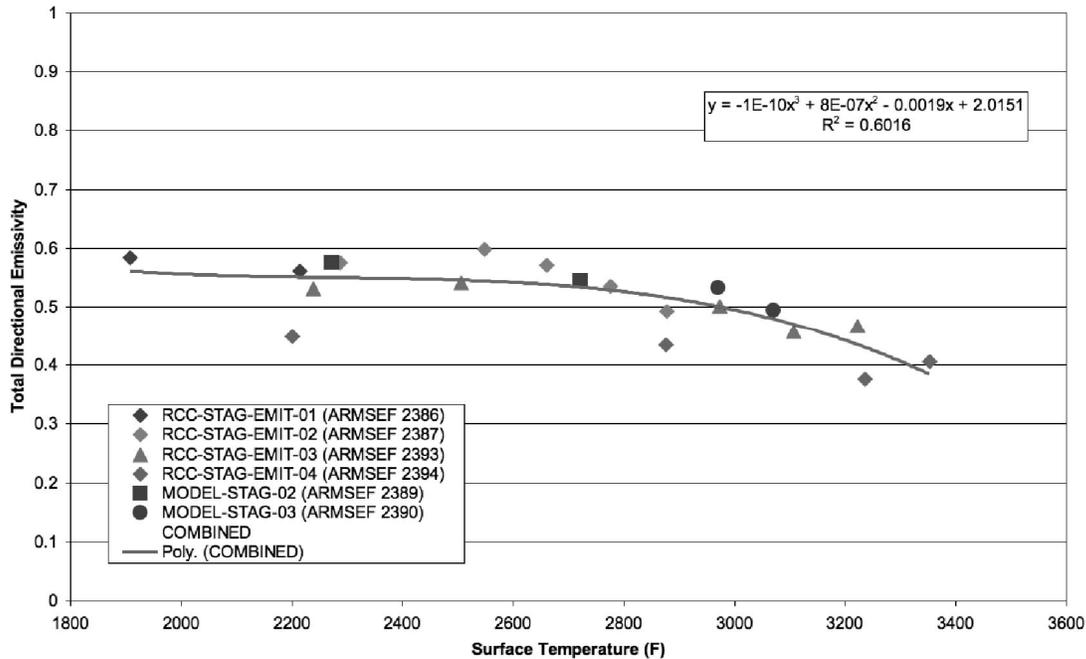


Figure 8. Variation of NOAX emissivity with temperature.

For the most part, emissivity ranged around 0.55 from 1900°F to 2600°F and trailed off to around 0.4 at 3350°F. At around 3000°F, the emissivity value is around 0.52 which is close to the design data point of 0.54 for RCC mentioned above.

SUMMARY AND CONCLUSIONS

Emissivity values have been measured on many oxidation-protection coating systems being investigated for use as TPS and hot structure using two different techniques. HfC/HfB₂ and Ir/HfO₂ 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 the Hafnium Carbide/Hafnium Diboride and Iridium/Hafnium Oxide coating systems provided for this study, unlikely candidates for leading-edge applications. These type of coating systems might become candidates, if their emittance could be raised.

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/HfB₂ and Ir/HfO₂ coatings, all other coating systems failed due to the development of a hot spot induced by 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.

At around 3000°F, the emissivity value of the NOAX paste-like material is close to the design data point for RCC.

The two coated C/SiC materials have different emissivities near 3000°F. Coating chemistry is a likely cause of this difference. The CVIP coating system had no appreciable change in emissivity through 7 thermal cycles. The trend of decreasing emissivity as temperature increases shown by the MCM-700 coating is similar to that shown in Figures 3 through 5 for other coating systems.

The uncoated C/SiC has higher emissivity than either of the coated C/SiC materials. The reason is unclear. It could be due to chemistry differences between the uncoated surface and the two coating. The fact that a different technique was used to measure the emissivity of the uncoated specimens than used for the coated specimens and the additional fact that the uncoated values are total normal data while the coated values are total directional, might also play a role in the difference.

The most recently measured emissivity data on RCC is much higher than the design RCC data and the data measured in Ref [3] at the higher temperatures.

The large scatter between measured data at high temperatures for both C/SiC and RCC using different techniques is troubling, and a more thorough round-robin research activity is required to establish confidence in various measurement techniques.

REFERENCES

1. Ohlhorst, C. W.; Vaughn, W. L.; Lewis, R. K.; and Milhoan, J. D.: "Arc Jet Results on Candidate High-Temperature," APS-II-77, JANNAF 27th Airbreathing Propulsion Meeting, Colorado Springs, CO., December 1-December 5, 2003.
2. Denaro, A.; Francesconi, D.; and Ramusat, G.: "FLPP Materials & Structures: Preparatory Development of Re-use and Re-Entry Technologies For Future Launchers," 5th European Workshop on Thermal Protection Systems and Hot Structures, Noordwijk, The Netherlands, May 17 – May 19, 2006.
3. Caram, J. M.; Bouslog, S. A.; and Cunnington, G. R. Jr.: "Emissivity Measurements of Space Shuttle Orbiter Reinforced Carbon-Carbon," AIAA 93-0841, 1993.
4. Rochelle, W. C.; Battley, H. H.; Grimaud, J. E.; Tillian, D. J.; Murray, L. P.; Lueke, W. J.; and Heaton, T. M.: "Orbiter TPS Development and Certification Testing At the NASA/JSC 10 MW Atmospheric Reentry Materials and Structures Evaluation Facility," AIAA-83-0147, January 1983.
5. Smith, D. M., E. J. Felderman, F. L. Shope, and J. A. Balboni, "Arc-Heated Facilities," Chapter 10, "Advanced Hypersonic Test Facilities" (Ed. F. K. Lu and D. E. Marren), AIAA Progress in Astronautics and Aeronautics, Vol. 198, American Institute of Aeronautics and Astronautics, Inc., Reston, VA., 2002.
6. Ohlhorst, C. W.; Glass, D. E.; Bruce, W. E. III; Lindell, M. C.; Vaughn, W. L.; Smith, R. W.; Dirling, R. B. Jr.; Hogenson, P. A.; Nichols, J. M.; Risner, N. W.; Thompson, D. R.; Kowbel, W.; Sullivan, B. J.; Koenig, J. R.; Cuneo, J. C.: "Development of X-43A Mach 10 Leading Edges," 56th International Astronautical Congress, Fukuoka, Japan, October, 2005, IAC-05-D2.5.06.
7. Williams, S. D.; and Curry, D. M.: "Thermal Protection Materials-Thermophysical Property Data," NASA RP 1289, December 1992.