METHODOLOGY, TECHNICAL APPROACH AND MEASUREMENT TECHNIQUES FOR TESTING OF TPM THERMAL PROTECTION MATERIALS IN IPM PLASMATRONS

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ABSTRACT

An induction plasmatron application for testing of thermal protection materials is discussed in presented paper on the basis of 35-years experience of Plasma Laboratory of IPM RAS. Metodology of testing of thermal protection materials in plasmatrons was based on simulation of hypersonic reentry heating near stagnation point using subsonic plasma jets, possibility to regulate pressure and flow enthalpy smoothly and independently of one another and the using of plasmatron's advantages such as purity of plasma flow, its high stability and reproducibility as well as wide ranges of realized pressure and heat flux. Purity of plasma flow allows to fulfill long-term aging tests (up to 100 15-minutes testing cycles for one sample) at excellent stability and reproducibility flow parameters. Conventional techniques of measurements and analysis such as pyrometry, SEM etc. are discussed together with developed approach to study of thermochemical stability of materials using complex application of optical spectral analysis, tests in different gases and methods of post test analysis.

1. INTRODUCTION: METODOLOGY AND TECHNICAL APPROACH

Induction plasma generators are the mostly suited to simulate aerodynamic heating of hypersonic vehicles when purity and stability of plasma flow are necessary to solve a problem in question. Owing to using contactless heating of gas flow by induction current, these facilities create exceptionally pure plasma flow of any gases as well as show high stability and excellent reproducibility of regimes. Last but not least advantage is a feasibility to make long-term aging tests in real time. Taken together, these advantages make induction plasma generators best suited to make aging tests of reusable thermal protection materials as it was shown in [1-3]. Besides, using of pure subsonic plasma jets make it feasible to simulate precisely such flight conditions as total enthalpy and pressure, a chemical composition and species distributions within boundary layer, heat flux, surface temperature, nonequilibrium gas-phase and surface reactions, i.e. thermochemical action of shock layer plasma on thermal protection materials near stagnation point.

Methodology and technical approach for testing of materials developed in IPM RAS includes the following items:
- testing of sample and full-scale elements of thermal protection system in stagnation point configuration, but if it is necessary to obtain very low heat flux or to test very large model one can use model arrangement at an angle of attack;
- development of test models to make fastening and heat insulation of rear side of sample as close to real vehicle as possible and to assure easy assembling/disassembling of model;
- choice of test regimes and making of preliminary tests using step-by-step heating;
- application of different test procedure (constant pressure and power, constant pressure and surface temperature or specified heating curve) for differently directed test campaigns;
- using of optical methods for surface temperature measurements;
- application of optical spectral analysis together with tests in different gases for investigation of thermochemical stability of reusable thermal protection materials.

Consider briefly above presented parts of technical approach, that was described in [4-6].

2. TEST CONFIGURATIONS

Two main test configurations are presented in Fig.1a,b (see next page). The first one is classical stagnation point configuration. Typical model diameters for 80 mm diameter of jet generated by plasmatron are in the range 45-60 mm. Stagnation point configuration is used both for aging tests and catalycity determination since it is convenient for numerical flow analysis. The second one is configuration with model arrangement at an angle of attack, that is used to test very large sample and/or to obtain very low heat flux to test model. To determine catalycity in this configuration one has to use rough models or to solve fulfill 3D Navier-Stokes problem. The greatest model ever tested in IPM using this configuration was of 525 mm diameter at 200 mm diameter of inlet section of discharge channel.
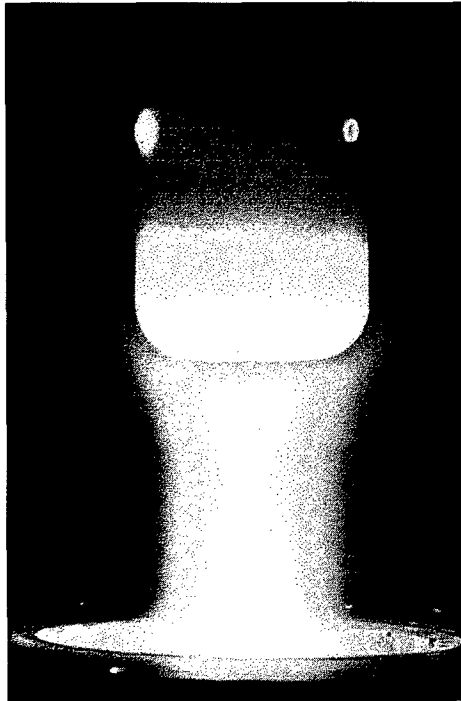
a)
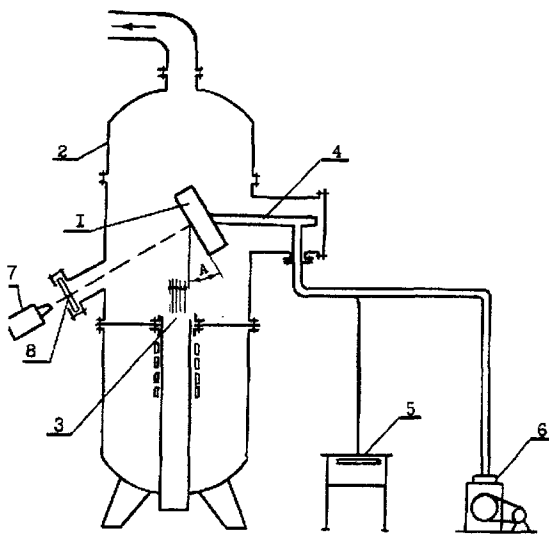
b)

Figure 1. *Test configurations: a − photo of test using stagnation point configuration, b − configuration of model arrangement at an angle of attack (1 - test model, 2 - test chamber, 3 - dissociated air flow, 4 - water-cooled holder, 5 - data loging system, 6 - vacuum pumps, infrared thermovision system, 8 - infrared window).*

3. SAMPLES AND MODELS

Conceptual sketch of test model used for sample testing since 1992 is shown on Fig.2. This model represents

flat faced cylinder of 50 mm diameter with edge rounded with 11.5 mm radius.
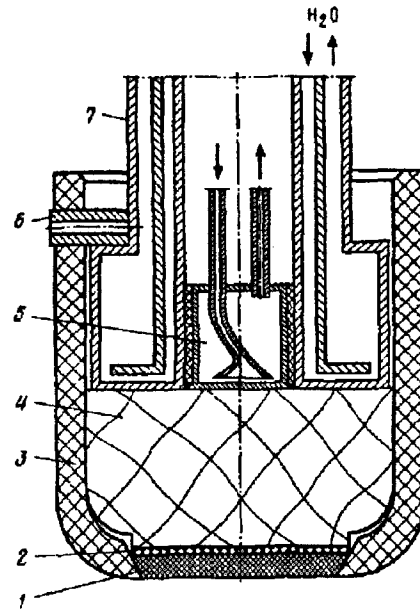
Figure 2. *Test model for aging and catalytic tests in stagnation point configuration. Test model for tests in stagnation point configuration. 1 - sample, 2 - spacer, 3 - mask, 4 - heat insulator, 5 - stationary water-cooled calorimeter, 6 - pin, 7 - water-cooled holder.*

Water-cooled stationary calorimeter is used for measurement of heat loss from rear side of sample to water-cooled holder and it allows to use heat balance to determine heat flux to hot surface that is necessary for catalycity determination.

Development of the models for testing of full-scale elements is individual complicated problem, since such model must meet very many requirements. Model is to be easy for manufacturing and as cheap as possible, simple in exploitation, easy for assembling/ disassembling. The only recommendation is to make design of heat insulation of rear side of a sample as close as possible to that one, which is used in real vehicle.

4. STEP-BY-STEP HEATING AS THE FIRST TEST OF NEW THERMAL PROTECTION MATERIAL

Method of step-by-step heating was used in experiments on a study of boundary layer spectrum before boiling of glass-silicide coating. This simple experiment is usually carried out in the very beginning of test program for a new material, since it allows to solve simultaneously a set of problems (calibration of used pyrometers, estimation of maximum operation temperature, quick comparison with previously tested

materials, etc.) in one 20-minute experiment. Essence of experiment is step-by-step change of power and as a result step-by-step heating of a sample up to its catastrophic destruction at constant pressure and mass flow of air. It is possible, since power, mass flow of gas and stagnation pressure are not linked among themselves in subsonic operation regimes of plasmatron and one can vary them independently of one another.

It is necessary to discuss this technique more carefully, because it plays special role in methodology of testing, used in IPM. First, such approach allows to create a database on dependencies of surface temperature against anode power for different coatings/materials tested under the same conditions of non-equilibrium heat transfer. As a rule, experiments are carried out at the same pressure 100 hPa and the same set of power levels is used and constant surface temperature is to be achieved on each "step". So, one can quickly compare obtained results with numerous data on previously tested materials and make conclusions concerned joint influence of surface catalycity and emissivity on sample temperature without any special individual careful studies of total emissivity and effective probability of a heterogeneous recombination as functions of temperature. Note, that these characteristic are known for some materials of database and such knowledge can be used for comparative study of new material.

Second, approximate temperature of the beginning of destruction allows to see potentialities of new material for high-temperature application, since maximum operation temperature depends in the main on used chemical system, but lifetime in the main depends on quality of technology of coating application

Third, character of kinetics of heating makes it possible to make conclusions about a possible direction of catalycity change during experiment. Typical kinetics of step by step heating is presented on Fig.3. Data were obtained using test stagnation point configuration. Temperature peak at constant power corresponds to catastrophic destrucion of sample. It is seen from Fig.3, that surface temperature decrease is observed during first steps at rather low temperatures of a sample on each "step". It can be caused by catalycity decrease or increase of coating emissivity, however, according available experience the first reason is significantly more probable, than second one.

The second relation, concerned step-by-step heating, is derived from power dependency of surface temperature and an example is given in Fig.4. It is interesting, that the long-term statistics accumulated in tests of ~100 various combinations "reusable C-C material/ antioxidative coating", that before the beginning of
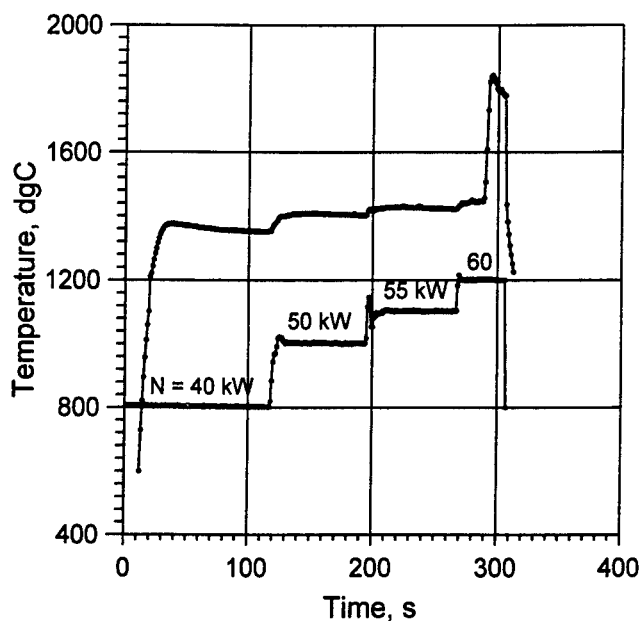

Figure 3. Time dependencies of surface temperature of gllass-silicide coating and anode power of generator.
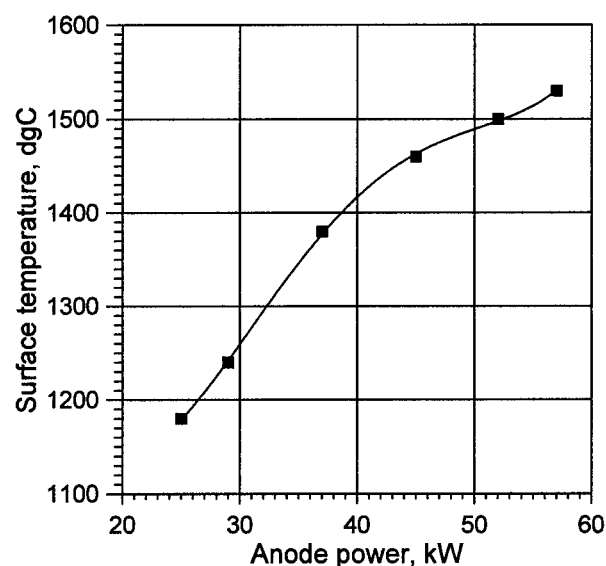
Figure 4. Surface temperature of tested sample with glass-silicide coating vs anode power of HF-generator.

catastrophic destruction the relation T(N) passes through a point of inflection. One of candidate reasons of the effect is heat effect of substrate oxidation, that is negligible at "low" temperatures, increases and becomes significant before the beginning of catastrophic destruction. Although exact explanation of discussed effect is not found yet, it has prognostic power and can be used in experimental practice to avoid catastrophic destruction, if it is necessary.

Step-by-step heating of sample was used in presented experiments together with recording of kinetics of boundary layer spectra on each «step».

5. MEASUREMENT TECHNIQUES

Mass loss of sample

This technique seems very simple and primitive. Really, accuracy of laboratory weighing is excellent. However, it makes it possible to observe water adsorption in porous materials etc. Practically, accuracy ~0.1-0.01 mg is enough. Real problem is to avoid sticking of sample and heat insulator (especially in cyclic tests). Very often spacer helps to solve this problem.

Commonly used samples for selective tests and research works are of disk form of 26.5 mm diameter with conical side surface as it is seen from Fig.2. However it is possible to use separable samples shown in Fig.5.
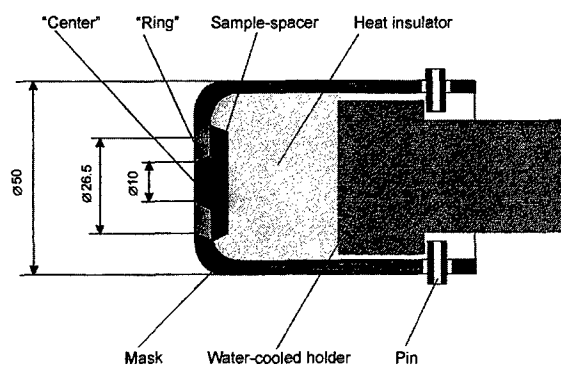
Figure 5. *Sketch of test model with eparable sample.*

A "separable" sample consists of two parts: a "center" with 10 mm diameter of front surface and 30° half angle of conical side surface is inserted into a "ring", so that the assembled "separable" sample has the same form and dimensions as the standard sample (thickness - 2.9 mm, diameter of front surface - 26.5 mm and half angle of conical side surface - 30°) and it can be mounted and tested in the same sample holder. Using "separable" samples made it possible to weigh individually the "center" and the "ring" between test cycles. Thus one can determine the mass loss rates in the central and peripheral parts of the sample. Note, that the ratio of the front surface areas of the "center" and the "ring" is about 1/6. It should be emphasized here that "separable" samples were proposed for experiments under conditions with significant mass loss because that allows to neglect mass loss/gain on the side and back surfaces of sample (or part of sample). That is why the mass loss rate was defined as the ratio of mass loss and front surface area of the sample. Before the main test program standard and "separated" samples were comparatively tested in order

to verify a possible influence of the sample's separation on its total mass loss and no significant difference was found.
Separable samples were used to show that mass loss rate is uniform over sample surface in subsonic tests, but it can be significantly non-uniform in supersonic tests and ratio edge/center can change about order of magnitude [6]

Surface temperature

Measurements of front surface temperatures of the samples, heated in induction plasma jet, were carried out using pyrometers. This choice is determined not only by problems of sensing element mounting into investigated samples, but by high-frequency interference from electromagnetic field of inductor as well as the problems in many times repeated assembling/disassembling of the model during aging tests. The first advantage of pyrometers is that pyrometry is contactless method of measurement. The second one is their universality, i.e. the opportunity to work with any kinds of materials, including highly specific materials like ceramic tiles and fibrous materials exposed to plasma flow. Generally recognized advantages of pyrometry are remained: pyrometry is contactless method and (if it is necessary) freedom from time-transit effects. However if it is necessary, thermocouples can be used (and they have been used) for measurement of temperature of rear side of a sample, temperature of some parts of test model, etc.

Optical pyrometer with disappearing filament POV-80 was used as the reference instrument for surface temperature measurements. This pyrometer, using standard wavelength $\lambda = 0.65$ μm, is characterized by high accuracy of brightness temperature measurement, simplicity of design and using.. Due to the optical system of 20^x magnification, pyrometer allows to observe the small details of sample surface, including sites of origins for thermochemical destruction of carbon-carbon materials with antioxidation coatings. The size of minimally small measured object is ~1 mm at the distance between object and pyrometer ~1 m.

The disadvantages of this device are impossibilities of continuous registration of temperature and of measurement of quickly changed temperatures as well as the necessity of the correction for spectral emissivity of an object and for spectral transmittance of optical window of vacuum chamber. The correction for the transmittance of vacuum chamber optical window and for sample spectral emissivity must be made using conventional formula. Spectral transmittance of optical window of test chamber was calculated using data on optical properties of used type of quartz and it was found $\tau = 0.935$ so this correction may be calculated

precisely. However the main error is of systematic nature. Its source is the error of emissivity, used in calculation of true temperature from brightness temperature. The accuracy of used optical pyrometer is so high (0,2% over 1400-2000°C temperature range and 0.15% over 800-1400°C), that error of brightness temperature measurements practically does not influence on the accuracy of true temperature determination.

The simplest way to estimate spectral emissivity of developed materials and coatings is to measure spectral reflection coefficient of a sample at room temperature and at wavelength used by pyrometer. It allows to find spectral emissivity from Kirchhoff law for nontransparent bodies: $\varepsilon_\lambda = 1 - R_\lambda$. Taking into account that at absence of chemical and phase changes $d\varepsilon_\lambda/dT$ is rarely more than 10K, it is acceptable to use values obtained using above mentioned way. Actually, optical pyrometer is not sensitive to spectral emissivity error. $\varepsilon_\lambda = 0.85$ was accepted for studied coating and for true surface temperature $T = 1300°C$ spectral emissivity error $\Delta\varepsilon_\lambda \sim 0.10$ leads to temperature error $\Delta T = 12°C$ and at $T = 1500°C$ - $\Delta T = 16°C$.

Partial radiation pyrometers with photoelectric sensors have been used in these tests when it was necessary to record data into computer memory. Used devices is equipped with silicon and germanium photodiode sensors. For these devices bands of sensitivity 0.5-1.1 μm and 0.7-1.6 μm respectively, temperature ranges: 600-1300°C and 1000-2000°C, accuracy: 1.5% and 1% (for exploitation at environment temperature - 40...+40°C, but when measuring in laboratory room at constant environment temperature it is to be better). The two devices with analog output 0-100 mV were used with multichannel digital recorder OPION-3500 and computer Pentium Pro 180. Response time of such system is determined by analog electronic circuit of pyrometer and its value is about 0.5-1 s.

Respectively large dimension of observed area (about 5 mm at 1 m distance between object and pyrometer) is of advantage or of disadvantage in accordance with situation. Insensitivity to plasma radiation is an advantage of these pyrometers in any case. The last fact is explained both by the increase of sample radiation at infrared range and by the decrease of plasma radiation at this range. Wide band of spectral sensitivity brings some additional difficulties into introducing the correction for object emissivity. Therefore corrections were made in real time during tests to make measured temperature equal to data of precision optical pyrometer corrected for spectral emissivity and transmittance of optical window. To establish necessary corrections calibrations of electronic

pyrometers using optical pyrometer were made in individual experiments with step by step heating of tested samples. Obtained corrections were constant during all test program.

Infrared thermovision system is another type of non-intrusive optical system for temperature measurements that was used for sample surface temperature.

The type of pyrometer is to be chosen as applied to the material under investigation. Sometimes this choice requires large work on "the agreement" of a pyrometer with an object. It should be taken into consideration not only temperature range, accuracy, minimal angle size of measured object, speed of response, i.e. technical performance data, which can be found in the specification, but the agreement of pyrometer spectral sensitivity with spectral emissivity of investigated materials and with spectrum of plasma radiation as well.

In many cases it is expedient to use pyrometers with spectral range, which agrees with the most intensive emission band of an object and does not agree with of intensive plasma radiation bands. The most simply, one can find emission bands by measuring spectral reflection coefficient p over wavelength range 1-15 μm, since for nontransparent materials Kirchhoff law can be written as $\varepsilon_\lambda = 1 - R_\lambda$

Unlikely, when the surface temperatures of plasma jet heated samples are measured, pyrometer spectral emissivity band has not to coincide with bands of intensive plasma jet radiation.

When testing ceramic heat protection tiles, thermovision system AGA-780 was in considerable use. This system is especially effective with the measurements of temperature of quartz as well as glasses and ceramics, based on silicon dioxide. It takes place because narrow-band filter, which is used in this device for measurements of high temperatures, has $\lambda_{eff} = 5$ μm, that corresponds with intensive absorption (and emission) band of above-mentioned materials. It is exceptionally important, that spectral emissivities of quartz and quartz-based ceramics on $\lambda_{eff} = 5$ μm are closed to 1, they are well known and practically nondependent on temperature (it is correct both for "black" and for "white" thermal protection tiles).

Since investigation of a ceramic tile was extensive, careful and prolonged, spectral emissivities of tile coatings have been measured carefully using special-purpose facilities (the Institute for High Temperatures of Russian Academy of Sciences et.al.). It allowed to make measurements of true surface temperature with high accuracy both in routine cyclic tests and in

experiments on non-standard heating. One of the most interesting works of the last type was the investigation of water-saturated tile behavior. It should be emphasized, that thermovisor gave the only opportunity to make this work, because highly nonuniform temperature distribution over investigated surface (600 < T<1300°C) varied with time quite guickly.

Simple evaluation shows, that extremely low reflection coefficient of quartz and of tile coatings at the wavelength 5 μm ($R_{\lambda=5\mu m}$ = 0.02) makes negligibly small the radiation reflected from surface and detected by thermovisor. It is true both for plasma space radiation and for radiation of heated up to few hundred degrees quartz discharge channel. Brightness temperature of plasma jet at λ_{eff} = 5 μm low and really it does not exceed 200°C, therefore direct plasma radiation along the optical axis of thermovisor also is very small and does not influence on the results of tile surface temperature measurements.

The correction for transmittance of vacuum chamber optical window is not small at thermovision measurement. However, using of BaF monocristalline optical window allows to calculate required value precisely, since optical characteristics of this material are known with high accuracy. It has been this material, which was chosen for it's moisture-resistance and transparence at visible band.

The calibration of thermovision system over temperature range 200-1500°C has been made in our laboratory by means of two specially designed absolutely° black body models. The first one was used at 800-1500°C (it was heated by 1 MW generator of the IPG-3 facility!) and the second one - at 200-1100°C. Optical pyrometer with disappearing filament POV-80 (T > 800°C), infrared pyrometer POI (400 < T 900°C) and specially calibrated Chromel-alumel thermocouple (200 < T < 1100°C) were used as reference devices. Results obtained by using of these two models showed excellent agreement. The error° of calibration is about 15°C.

In closing, it should be noted, that, when measuring other materials, for example, based on Al_2O_3, the employment of this thermovision system is not so far effective as in the case of ceramic tiles with silicate or borosilicate coatings. It lakes place, because emissivity of Al_2O_3 at used wavelength 5 μm is known with poor accuracy, but results of true temperature calculation are sensitive to emissivity errors. For instance, at measured brightness temperature T = 1200°C, the error in emissivity ~0.05 leads to error ~40°C. The accuracy, as poor as above-mentioned, is sufficient usually and very often this disadvantage is not balanced out by

opportunity to measure the time-dependence of temperature field over whole front surface of a sample.

Surface morphology

Surface morphology is very informative and photography of sample one can find in any report or article. Additionally, scanning electron microscopy (SEM) is excellent method for using after test campaign. Note, that to get pictures of samples with bad electrical conductivity one has to deposit thin gold film on studied surface. It is useful to obtained not only usual photos but photos of sections and two SEM photos of the same coating of ceramic tile.


a)
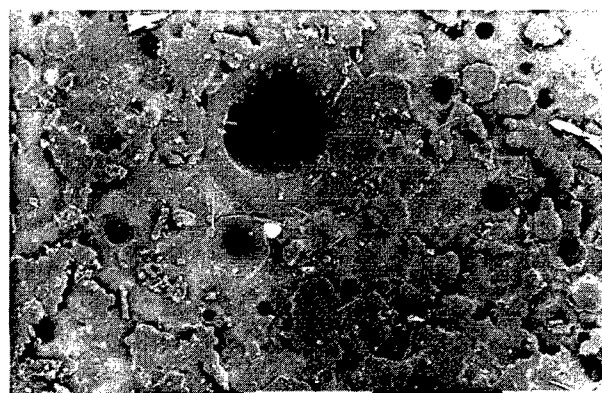
b)

Figure 6. SEM photos of thermal protection tile coating; a – surface, b - section.

One can see that section gives more informative picture.

Residual strength

Residual strength has been used for study of carbon-carbon and tile materials after testing. Fig.7 shows results of residual bending strength measurements for carbon-carbon samples of 84 mm diameter, which withstood 1, 3, 10, 30 cycles at 1480°C in the IPG-3 facility.
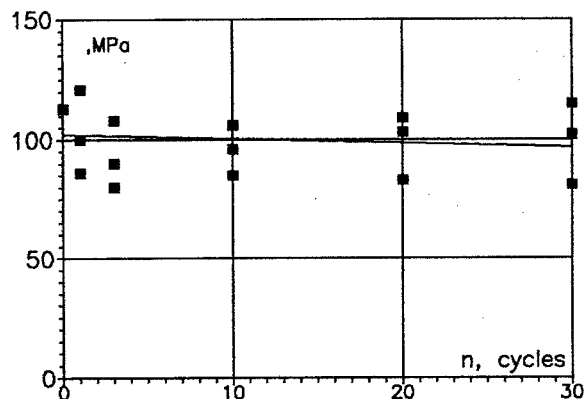
Figure 7. Residual bending strength of siliconized C-C material with glass-silicide coating after 3 10, 20, 30 testing cycles at 1480°C.

Otherwise, tile material is tested for tension residual strength, since this type of loading is the most dangerous for tile material.

6. TEST PROCEDURE

Test procedure described below is typical and it was used in real study of SiC reference material oxidation which was made for ESTEC/ESA [4-6].

Preparation to test.
1. Checking of coincidence of masks and samples.
2. Weighting of the samples.
3. Photographing of front and back side of each samples.
4. Visual inspection of surface of each sample using microscope. Description of observed details.
5. Classifying of the samples into two groups: (i) for pretests and calibration and (ii) for main test program.
6. Measuring of spectral reflection coefficient of each sample in the range 0.3-2.5 mm at room temperature.
7. Measuring of total emissivity of each sample at room temperature.
8. Measuring of temperature dependence of reflection coefficient $\lambda = 0.6328$ μm for SiC and graphite materials at room temperature.

Calibration and test conditions measurements in the IPG-4 plasmatron of IPM.
1. At constant air mass flow through discharge channel and at constant pressure in test chamber, which is equal to specified total pressure, dependence of steady-state sample temperature versus RF-generator power is to be measured during step by step heating of a sample. Power levels, which are necessary to achieve specified temperatures are determined by interpolation. Also these series of experiments are used to calibrate using recording pyrometer by reference optical pyrometer with $\lambda = 0.65$ mm. Obtained corrections as well as correction for spectral emissivity (based on data of point 1.6) are taken into account by computer system during test cycles.
2. Taking into consideration (i) very weak pressure dependence of sample temperature and (ii) the fact that dynamic pressure is significantly less than total pressure, test chamber pressure which is corresponded to specified total pressure is determined in individual experiments with Pitot tube. Also these experiments are used to measure dynamic pressure and hence to determine flow velocity.
3. Checking of regimes validity is made by measuring sample temperature at established test chamber pressure and generator power. Measurements of heat fluxes and plasma flow parameters for all regimes are made after calibration and before tests. Required number of samples is equal to the number of used regimes + four samples for calibration, pretests and reserve.
4. The following parameters are to be measured for each selected regime:
- heat flux to water-cooled flux-meter of the form identical with that one of tested model,
- enthalpy (is computed using heat flux measurements to high catalytic cold wall),
- dynamic pressure,
- pressure in test chamber.

Tests cycle.

The following parameters are recorded during each cycle:
- temperature of front surface of a sample (with correction for spectral emissivity),
- pressure in test chamber, - heat flux from back side of a sample,
- temperature dependency of reflection coefficient of a sample at $\lambda = 0.6328$ mm during heating.
- power in anode circuit of RF-generator.
- repressuration of the test chamber at sample surface is to be made after temperature below 400 C.

After each cycle the following measurements and actions are to be made:
disassembling of test model and visual inspection of all details and sample; damaged details are replaced, measuring of mass loss per cycle,

measuring of spectral reflection coefficient of front side in the range 0.3-2.5 μm at room temperature,
measuring of total emissivity of front side at room temperature,
photographing of front and back side of a sample (Polaroid, two copies),
assembling of the model for next cycle.

7. STUDIES OF THERMOCHEMICAL INTERACTION BETWEEN PLASMA AND MATERIAL

**Pressure and temperature dependencies of mass loss rate**

Temperature and pressure dependencies of mass loss rate were obtained using the IPG-2 facility. Pressure dependence of mass loss rate averaged over four 10-minutes cycles at $T_w = 1480^{\circ}C$ is given in Fig.8. The dependence found is linear in lgP - lgG coordinates, so $G(P) = A \cdot P^B$. Least square method gives $G(P) \sim P^{-0.19}$, that suggests the coating is gas-tight, since Medford established that $m(P) \sim P^{0.8}$ [7,8] when free molecular diffusion of oxygen through pores and fissues is the main mechanism, defining mass loss rate. It should be emphasized that two facilities, – the IPG-2 and IPG-3, – were used to obtain pressure dependence but since 1989 such experiment may be realized using only IPG-4 facility which allows operation in uniquely wide pressure range.
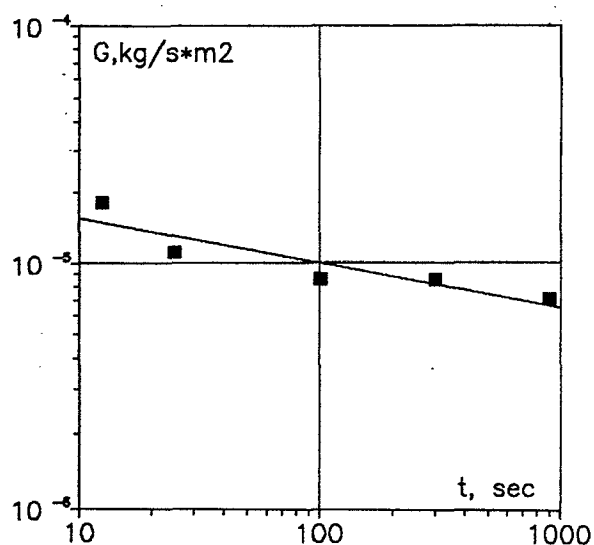
Figure 8. *Pressure dependency of mass loss rate of carbon-carbon material with antioxidative glass-silicide coating.*

Mass loss rate versus inverse absolute temperature is shown in Fig.9. Data on mass loss rate at pressure P = 100 hPa were averaged over six 10-minutes testing cycles. Mass loss rate for carbon-carbon material

without any antioxidation protection are presented in Fig.12 to make visible the effect of antioxidation coating deposition. Sharp increase of temperature is caused by the effect of "boiling" of the coating.
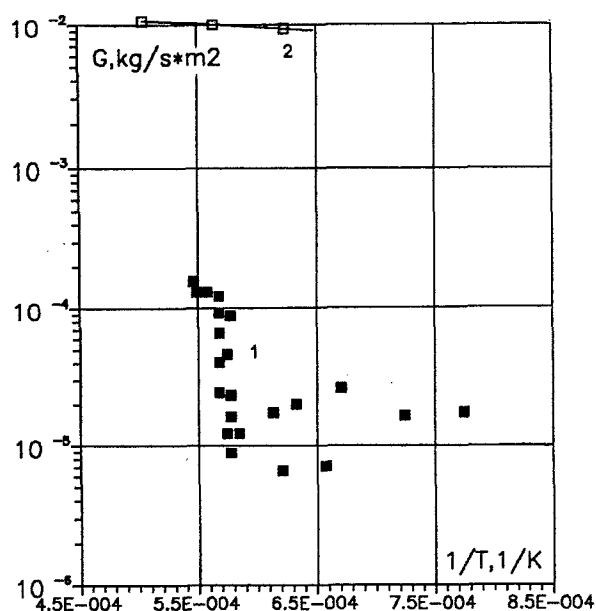
Figure 9. *Temperature dependency of mass loss rate of carbon-carbon material with antioxidative glass-silicide coating. 1 - tested material, 2 carbon carbon material without any antioxidation protection.*
spectra

Thermochemical stability of reusable TPM

Thermochemical stability of reusable material is its important characteristics. It is ability of material to withstand concurrent influence of high temperature and chemically active components of initial flow (primarily atomic oxygen). In practice a thermochemical stability is estimated by number of test cycles (or total time) without impermissible degradation of strength, emissivity, catalycity of material under simulated reentry conditions in real time scale.

Carbon-carbon materials are in considerable use in aerospace vehicles due to their unique characteristics. High strength, low specific weight, stability of thin-walled structures of large size under thermal shock and the opportunity to make design elements with beforehand specified properties with maximum strength along direction of maximum load make carbon-carbon using highly attractive for designers. Carbon-carbon materials have high friction properties and they are also biologically inert.

When using carbon-carbon materials as reusable thermal protection materials, it is of great importance that, unlike metals and alloys, the strength of carbon-

carbon materials increases with temperature in gradual manner so that the value at T ~ 2200°C is nearly twice as large as this one at room temperature. Therefore at the preset time maximum exploitation temperature and life time of materials on hand under reentry conditions are limited by the quality of antioxidation coating, which is to prevent carbon-carbon substrate from oxygen access. Concurrently a coating is to the multi-purpose and to meet a number of requirements on emissivity, catalycity, hydrophoby, gas-permeability, coefficient of thermal expansion.

An analysis showed, that the following parameters are to be measured during tests or after them: mass loss and morphology of sample surface, after each cycle of testing, residual flexural strength and gas-permeability coefficient after tests. Surface catalycity and emissivity are also of importance for reusable thermal protection materials used on hypersonic vehicles.

Of special importance for carbon-carbon materials with antioxidation coating but without any oxidation protection in material volume is the formation of destruction zones, since their formation often is the beginning of catastrophic destruction of a sample, or at best is the forerunner of this process. Therefore if tested material may come to catastrophic destruction it is important to find the forerunners of the formation of destruction zones and the reasons of their formation.

General criteria of thermochemical stability estimation are in our opinion as follows:
- decrease of residual strength below specified value;
- occurrence of destruction zones of hazard dimensions.

General parameters, which are to be monitored during or after tests are:
- sample temperature as a function of time at constant parameters of initial plasma flow;
- morphology of sample surface;
- mass loss as a function of the number of test cycles.

Acceptable values of flexural strength decrease, of closely related with it mass loss and of dimensions of destruction zones are to be determined individually for each specific material and specific exploitation conditions.

When testing extensively thermal protection material or hypersonic vehicle, it is also appropriate to make:
- chemical analysis of a sample before and after test using one of recent contactless methods;
- measurements of gas-permeability coefficient of samples coating in initial state and after test.

In conclusion it should be emphasized, that nowadays there is no universal method to estimate a thermochemical stability of carbon-carbon materials with antioxidation coating. It is caused by the fact that tolerable changes of material characteristics essentially depend on used combination coating/substrate. Moreover, these tolerable changes may be different for the same material under different exploitation conditions.

For example, consider carbon-carbon material with he coating based on SiC and without additional oxidative protection in material volume. At temperatures 1600-1700°C, which are maximally permissible for such coating, the formation of destruction zone with following catastrophic destruction is the most dangerous. Unlikely, at respectively low temperatures ~1200-1400°C the decrease of strength as a result of carbon-carbon substrate oxidation is of greatest hazard to the same material. One may find even total oxidation of substrate as it has been obtained in one of 100-cycle test in our laboratory.

Optical spectral analysis is one of the most promising methods for the study of plasma action on reusable/non-ablative thermal protection materials (TPM). Its application makes it possible to observe *in situ* degradation of antioxidation coatings during aging tests in plasmatron, since analysis of boundary layer spectrum permits to find, what kinds of species are at a loss from substrate/coating during test, to see time dependencies of those losses *etc*.

For some other combinations of C-C materials and antioxidative coatings it was found, that after catastrophic destruction during oxidation tests one can find only strongly damaged pieces instead of sample. Note, that when coating contains large mass percent of oxididazable species, increase of surface temperature will cause heavy oxidation sooner or later and large amount of produced heat will result very quick transition from quasi-stationary regime to intense burning, i.e. catastrophic destruction. So, to avoid quick catastrophic destruction is important not only in real flight, but in ground tests, too. Really, very often thermochemical stability of large samples or full-scaled elements is lower, than it was found in testing of small samples, but it is very desirable to save expensive and deficit samples for post-test analysis.

Optical spectra analysis is one of the most promising techniques for investigation of physiochemical action of high enthalpy flow on thermal protection materials.

In experimental reentry simulation optical spectra analysis was used not only for plasma diagnostics of high enthalpy jets but for study of plasma-material interaction. The following problems were solved using this method in the investigations of ablative materials:

- qualitative analysis of chemical composition of thermal destruction products;
- quantitative analysis of chemical composition of thermal destruction products including concentration distribution of different atoms, molecules and ions;
- measurements of temperature distribution across the boundary layer including analysis of local thermal equilibrium in the boundary layer using measurements of translation, rotation and vibration temperatures as well as the measurements of atomic lines exitation temperature;
- determination of absorption coefficients and emissivity of destruction products.

These investigation were carried out under large blowing parameter $B = \rho_w v_w / \rho_\infty v_\infty > 0.5$ when mass flow rate of destruction products is compared with mass flow rate in initial plasma jet. In that case vapor concentrations are great and the radiation intensity of destruction products is orders of magnitude greater than that of pure plasma of initial flow.

When testing reusable thermal protection materials the situation became exactly opposite. All observed spectrum of destruction products may consist of a few atomic lines . As a rule they are sensitive lines of different atoms. Two exceptions are possible. 10, 20 or more lines may be observed when atoms of heavy metals such as molibdenum, tungsten, zirconium etc. come to boundary layer from the surface or when those are generated by disoociation of molecules . The other possibility is realized when far great mass loss rate occurs for materials under extreme, nonstandard conditions and for bad materials. It should be emphasized that it is rather difficult to find molecular bands in spectra of destruction products even if the presence of some molecules in boundary layer is obvious (for example, SiO molecules near SiO_2 surface heated to 1100^oC).

Although optical spectra of destruction products of reusable thermal protection materials are "poor" (in contrast to "rich" spectra of destruction products of ablative materals), they give reasonably good possibilities to study physiochemistry of plasma-material interaction. Although there is no need to study absorption coefficients of destruction products and it is impossible to measure temperature distribution near the surface since temperature gradient near surface is far too large, there is sufficient number of useful feasibilities. For example it is possible to determine ratio of component concentrations in boundary layer using coincidences of exitaion energy of spectral lines of different atoms. For example, it is feasible in practically important case of silicon and boron atoms (Ref.10). The other attractive feasibility is connected with small mass loss rate of reusable materials. This is

small mass rate that leads to diffusion of gaseous products of oxidation and vapor components across boundary layer instead of blowing of destruction products for ablative materials. It may be shown that under some assumptions mass loss rate of the component is directly proportional to total intensity of its spectral lines over boundary layer. It makes the especially attractive to study time dependencies of atomic lines intensities. Of coarse, qualitative chemical analysis of boundary layer composition is kept of importance. In any case optical spectra analysis is the only simple and inexpensive technique that allows to study thermochemical behavior of reusable thermal protection materials in situ over cyclic aging tests of arbitrary duration without any special preparation of samples.

It is evident that applications of optical spectra analysis for the study of thermochemical action on reusable thermal protection materials by dissociated air jets merit essentially more detailed consideration but here it is sufficient to emphasize that all above mentioned feasibilities may be made more powerful in combination with making tests in different plasma environments such as air, nitrogen, oxygen and argon.

The scheme of experimental setup [9], used for a study of emission spectra of boundary layer on tested samples, is presented in the Fig.10.
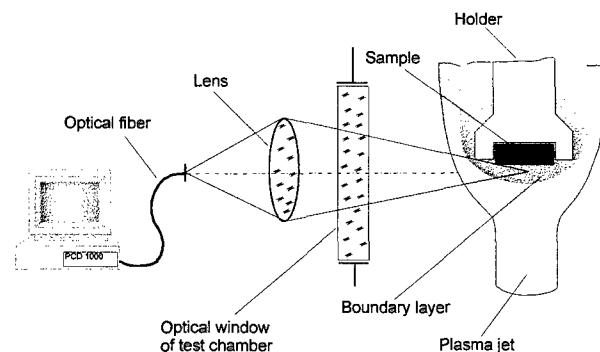
Figure 10. Conceptual sketch of experimental setup for spectral study of boundary layer on tested samples.

The main element of the setup is the plug-in computer dual spectrometer PCD 1000, that works in spectral range 200 - 950 nm. The one of the spectrometers works in the range 200 - 450 nm, has 25 μm input slit and its resolution is about 1 nm, the other works in the range 450 -950 nm with resolution ~3 nm, a fiber output cross section serves as its input slit. The optical fibers of 50 μm diameter are used to direct the emission to the spectrometers. The quartz lens of 120 mm focus, used in the setup, creates on the fiber input the 4 times reduced image of the central section of plasma jet. It means, that in the range 200 - 450 nm the emission is taken from the plasma jet area of $0.1x0.2$ mm^2, but in

the range 450 -950 nm - from the area of 0.2x0.2 mm^2. Note, that only intensive doublets of atomic sodium and potassium were found in long wave band but the most interesting lines are grouped in short wave band, so only short wave spectrometer was used practically in all experiments.

Since 1963 spectrometers with difractional gratings and focal length 3 m and 1 m were used for spectra registration using photo plates and photomultipliers. Now CCD-camera with 1024x1024 matrix can be used for careful experiments with high spectral resolution and spatial resolution across boundary layer.

Spectral precursors of catastrophic destruction

Spectral precursors of catastrophic destruction were observed in tests of C-C material with glass-silicide antioxidative coating. The most interesting zone of spectrum of boundary layer over glass-silicide coating is shown in Figure 11. The most important atomic lines, which are appeared in emission spectrum of boundary layer due to coating degradation, are sensitive (last) lines of atomic molybdenum, silicon and boron and those are shown in the Figure 11. Also there is some number of relatively weak lines of atomic molybdenum as well as lines of manganese, sodium and potassium, which present in the coating in small concentrations. However,
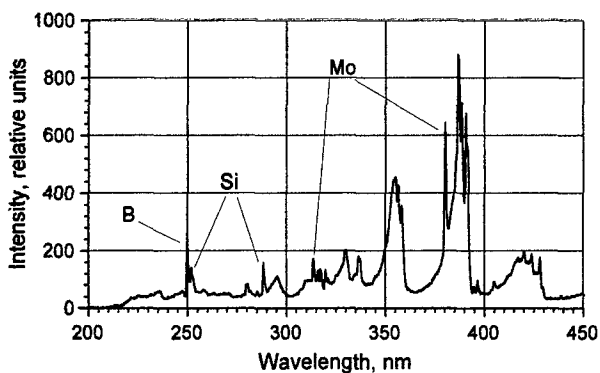

Figure 11. Spectrum of boundary layer over glass-silicide coating.

lines,because, as one can see from Figure 11, radiation of hot flow over a model is recorded by spectrometer, too, although it is less intensive, than spectrum of free jet, but it is more intensive, than it is possible to expect for boundary layer.

It was found, that intensities of molybdenum lines become unstable before the beginning of catastrophic destruction, but at the same time intensities of other lines of main components of the coating such as silicon and boron don't demonstrate such behavior. Typical variation of molybdenum lines intensities is shown in Figure 12 with time between the two recordings is

0.4 s, but to have more precise picture it is necessary to see kinetics of changing of basic parameters.
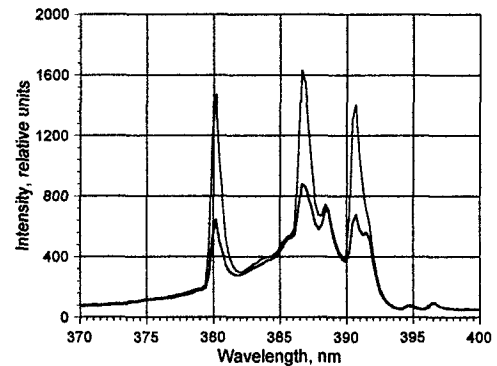
Figure 12. Fragments of two spectra of boundary layer on glass-silicide coating recorded with delay 0.4 s.
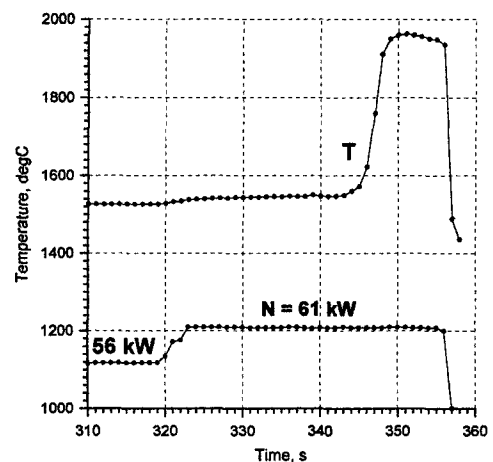
Figure 13. Time dependencies of sample's surface temperature and generator's anode power before catastrophic destruction («boiling»).
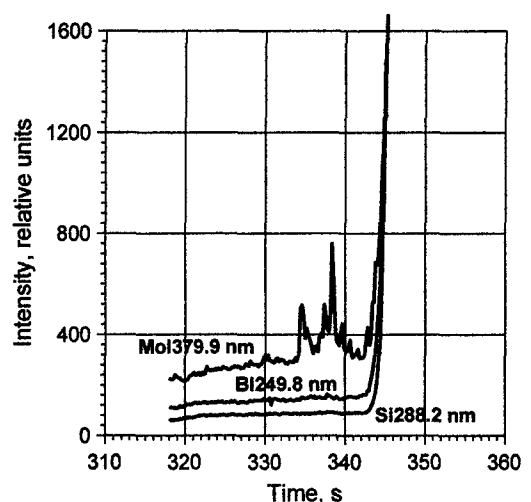
Figure 14. Time dependencies of sensitive lines intensities of different atoms which appeared in boundary layer due to coating degradation.

Time dependency of surface temperature of glass-silicide coating is shown on Figure 13 together with anode power of HF-generator before the beginning of boiling, and time-dependencies of intensities of sensitive lines of a molybdenum, boron and silicon are submitted on Figure 14 for the same test. As it is seen from Figures 13, 14, intensities of lines of silicon and boron before the beginning of boiling are enough stable and those begin to increase only with the increase of surface temperature. At the same time intensity of molybdenum line begin to pulse ~10 s before the beginning of «boiling». Peak intensities can be 2-3 times higher than its quasi-stationary level. There is no such peaks at usual operating temperatures, they appear only before «boiling». This result is in a good agreement with previous data on physico-chemical mechanism of «boiling»: it is caused by intensive oxidation of $MoSi_2$ particles, containing in the coating, by atomic oxygen from oncoming flow [2,3]. At the same time observable peaks shows, that before boiling heavy oxidation is blocked time by time with formation of protective film of oxides, and only then it becomes such strong, that the formation of film does not realized. So, study of specific features in behaviour of boundary layer over tested sample before catastrophic destruction allowed to obtain new information on mechanism of destruction even for well-known material & coating. Of coarse, such study can be more fruitful for new TPM and/or coatings.

Thus, it was found, that before boiling one can find few peaks of molybdenum lines intensity. There is no such peaks at usual operating temperatures. Repeatability in appearance of those peaks before «boiling» allows to consider them as «spectral precursors» of catastrophic destruction.
It is obviously, that boiling of glass-silicide coating is only one of many possible kinds of catastrophic destruction. However, it is more possible to find precursors when oxidizable components is exposed to dissociated air before the beginning of catastrophic destruction. Such situation can be found with multilayer and multiphase coatings, containing components, which can be oxidized with production of large amount of heat.

Other types of antioxidation coatings applied on C-C materials were preliminary tested to find spectral precursor of catastrophic destruction. The first results showed, that tested coating is not the only coating with spectral precursors of catastrophic destruction and there are different types of spectrum behavior before destruction. At the same time first attempts to find spectral precursors were not successful with the carbon-carbon samples with SiC-based coating. However, it means only, that searches are to be continued.

Study of spectral precursors of catastrophic destruction can be easily made practically in each laboratory, working on TPM testing in plasma jets. First of all, it can give important information about physico-chemical processes, that initiate catastrophic destruction of tested reusable TPM. Of coarse, that information can be used to refine chemical composition and technology of coating and, hence, to remove the beginning of catastrophic destruction to higher temperatures.

Besides, it is well known, that scale factor is very important for thermochemical stability of samples and full-scale elements of carbon-carbon materials with antioxidation coatings, which are used for oxidation tests, because usually it is difficult to realize on full-scale elements the same level of thermochemical stability, that has been demonstrated in tests of small samples. Knowledge about spectral precursors of catastrophic destruction can be used fruitfully to save expensive large samples and/or full scale elements from catastrophic destruction in plasma jet tests and to have an opportunity to make after-test analysis of substrate and coating exposed to extreme thermochemical loading. Actually, if one knows what kind of spectral precursor type takes place on material/coating on hand, it is not too difficult to develop special code to produce signal for test interruption (or for decrease of power put in plasma), when precursors appears in spectrum.

Tests in different gases

Many essential features of thermochemical action on thermal protection material by dissociated air flow may be found using optical spectra analysis in combination with making tests in different plasma environments such as air, nitrogen, oxygen and argon. As a rule mass loss of carbon-carbon materials with antyoxidation coating is generally resulted from the oxidation but atomic oxygen is essentially more active than molecular. Comparative study of optical spectra of boundary layer allows to understand what components is arised in boundary layer due to thermal vaporization and what components is arised in boundary layer due to thermochemical action of the initial flow. Obviously, above mentioned approach is to be combined with data on temperature, pressure and time dependencies of mass loss rate, as well as photos of surface obtained using SEM etc.

Emission optical spectra were obtained during tests in dissociated air and nitrogen flows. All experiments were carried out at constant pressure P = 100 hPa using the IPG-4 facility. More than 20 rather intensive spectral lines of molybdenum were found when sample was exposed to dissociated air flow. Also sensitive lines of BI, SiI, MnI, KI, NaI were observed in

boundary layer overflowed by dissociated air flow. Note, that simple qualitative chemical analysis gives two interesting results. The observation of molybdenum lines alone is the result of great importance for the understanding of thermochemical action of dissociated air on the glass-silicide coating.

Specially made plasma jet tests showed that there are no even weak sensitive lines of molybdenum while dissociated nitrogen overflowed the sample but lines NaI, KI, BI, SiI were found in these spectra. These result suggest that molibdenum atoms arising is caused by the thermochemical action of oxygen but the other components arise in boundary layer due to thermal evaporation. Taking into account that back side of tested sample which was exposed to non-dissociated air practically at the same pressure and temperature (since tests were made in subsonic flow and back side was heat insulated), one can make conclusion that it is atomic oxygen that causes such damages to coating. The most effective way of molybdenum loss is associated with the oxidation of $MoSi_2$ followed by evaporation of exceptionally volatile molybdenum oxides and it is one of the leading mass loss processes.

CONCLUSION

Effective test methods were developed for reusable thermal protection materials on the basis of plasmatron advantages and subsonic modeling of hypersonic heating. Complex approach, which includes tests in maximally wide pressure and temperature ranges together with tests in different gases and optical spectral analysis application, showed its efficiency for a study of thermochemical stability of reusable materials and physico-chemical mechanisms of plasma-material interaction.

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