INVESTIGATION OF THE EROSION BEHAVIOR OF GRAPHITE AND SILICON CARBIDE BY MASS SPECTROMETRY

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Abstract

Before their application heat shield materials for thermal protection systems of space vehicles have to be tested in ground based facilities under re-entry conditions. For this purpose, different plasma wind tunnels are in use at the Space Systems Institute (IRS) at Stuttgart University. In one of them investigations of the erosion behavior of graphite and silicon carbide, the basic materials for ceramic heat shields, have been executed by means of mass spectrometry. The material samples were exposed to different high enthalpy plasmas. Using graphite samples, CO and CO_2 could be detected. With SiC no erosion products could be found so far at the investigated pressure and temperature levels.

INTRODUCTION

Space vehicles entering the atmosphere of a celestial body are exposed to severe heat loads and chemical aggressive environments leading to high surface temperatures and erosion of their thermal protection systems. The IRS plasma wind tunnels (PWK) were designed to simulate the early entry phase of space vehicles into the upper atmosphere. The plasmas are generated either with magnetoplasmadynamic sources [1] or with a radio frequency source [2]. For re-usable space vehicles the thermal protection shields have to withstand the aggressive re-entry conditions several times. Therefore, ceramic materials based on graphite and silicon carbide are in use. Quite frequently these are fiber re-inforced C/SiC or C/C materials with a protective coating. It is of great interest to determine under which conditions such protective coatings fail and the erosion of the material underneath starts. The mass spectrometry is one method to determine such a failure on-line by the detection of the erosion products.

TEST FACILITIES

The Plasma Wind Tunnel PWK2

The mass spectrometric investigations were performed in the plasma wind tunnel PWK2. This facility consists of a water cooled vacuum tank with a diameter of 2 m and a length of 5 m. It is equipped with a magnetoplasmadynamic generator, in which the different gases are heated by an electric arc between a glowing tungsten cathode in the combustion chamber and the last segment of the accelerating nozzle serving as an anode. The arc current can be varied between 200 A and 4 kA, corresponding to a power between 40 kW and 1 MW. The mass flow rates are up to 30 g/s of different gases like N_2, O_2, Ar, H_2 or CH_4. In the case of a re-entry simulation the plasma is composed of N_2 and O_2 and -under certain operating conditions- Ar to avoid spotty attachment of the electric arc and destruction of the anode. The specific enthalpies range from 2 MJ/kg to 150 MJ/kg. PWK2 is equipped with a platform on which the probes can be positioned at different distances to the plasma source and can be moved perpendicularly to the plasma jet. Because of the high heat loads in the PWK the plasma source, the platform and the probes are cooled with high pressure water.
The IRS laboratory is equipped with a powerful vacuum system with a total suction capacity of about 300 000 m^3/h at 0.1 mbar. The minimal pressure inside the vacuum tank is less than 0.1 mbar and can be varied up to higher pressures. The high current power supply provides a power up to 6 MW with a maximum current of 48 kA or a maximum voltage of 6000 V.
The required test conditions are controlled by regulating the parameters ambient pressure, arc current, mass flow rate and distance of the probe to the plasma source.

For the characterization of the plasmas different measurement techniques are in use [3]: Heat flux and Pitot probes, electrostatic probes, and a mass spectrometer can be installed inside the PWK. Optical methods like emission spectroscopy and Fabry-Perot-interferometry are used as non-intrusive diagnostic methods. For the determination of material sample temperatures either thermocouples or pyrometers are in use.

The Mass Spectrometer

The mass spectrometer allows the measurement of neutral particles and ions as well as their energy distributions [4]. It consists of the following parts (see Fig. 1):

Ion source: For the analysis by electromagnetic fields the neutral particles entering the mass spectrometer first have to be ionized. This is done by electron impact ionization (electron energy usually about 70 eV). By the impact the neutrals often are not only ionized but also dissociated. If external ions are to be measured, the ion source has to be switched off.

Energy analyzer: The energy analyzer, an "cylindrical mirror analyzer", determines the energy distribution of external ions. The operating range covers 0-50 eV or 0-500 eV.

Mass analyzer: The particles are selected by a "triple filter quadrupole" according to their mass-to-charge ratio by a high frequency electric field. The operating range is up to 300 atomic mass units (amu) with a resolution of about 1 amu.

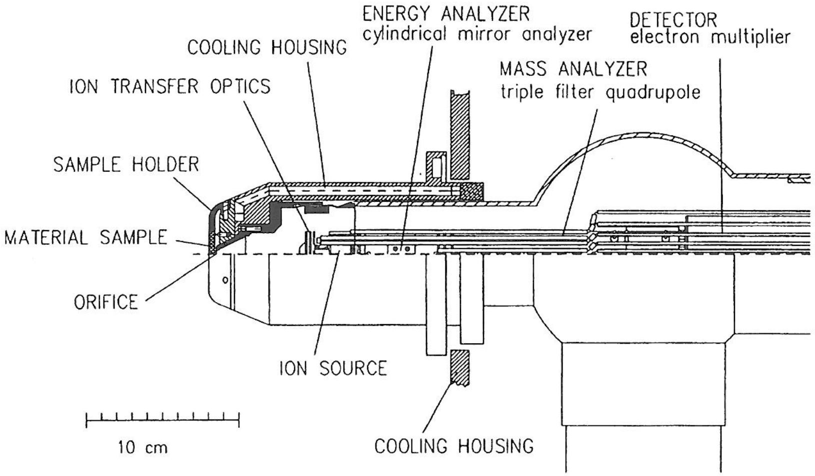

Fig. 1: Cross section of the mass spectrometer

Detector: An electron multiplier is used as detector system. Here the particles are collected and the signal is amplified by electron multiplication.

Ion transfer optics: Different electrostatic lenses focus the ion beam. The potential selected for the entrance optics decides, whether neutrals or positive or negative ions enter the mass spectrometer.

Orifice: To keep the pressure inside the mass spectrometer beyond $4 \cdot 10^{-6}$ mbar the particles have to pass through an orifice with an opening diameter of about 40-100 µm, depending on the total pressure in front of it. The high vacuum is necessary not only to prevent damage from the electron multiplier but also to avoid interactions between particles inside the device. To get a particle gain as high as possible and to keep the influence of the particles' interactions with the walls low, the length-to-diameter-ratio of the orifice opening should not exceed 1 [5]. To meet this requirement, it is made from tantalum foil.

For the measurement of erosion products the material samples are fixed directly in front of the orifice and are only cooled by radiation. To let the particles pass through to the orifice there is a hole (diameter: 2 mm) in the middle of the samples, which have a thickness of up to 4 mm. The dimensions of the sample holder and the specimen are chosen similar to the material and mechanical probes used for material qualification to ensure the comparability. During the tests the front side temperature of the samples is measured by a linear pyrometer.

The mass spectrometer is placed inside the PWK2 on the movable platform. The turbo pump is also located inside the vacuum tank. The connections to the electronics of the pumping system and the spectrometer on the outside of the tank are fed through a bellow. Because of the severe heat loads inside the plasma jet, a special cooling housing provided with high pressure water is necessary.

EXPERIMENTS

In the following measurements of neutral particles are shown behind samples of graphite and silicon carbide in two different plasmas. One is a nitrogen/oxygen plasma at an ambient pressure of 2.9 mbar, where the C-sample reached a temperature of 1270°C, the other is an argon/oxygen plasma at 1.75 mbar, where the sample temperatures were 1100°C for C and 1050°C for SiC, respectively.

RESULTS AND DISCUSSION

Fig. 2 shows three mass scans of neutral particles behind a graphite sample in an N_2/O_2-plasma. One scan is taken outside the plasma jet with a cold sample, one inside the jet during the heating phase, and one with the hot sample at a stationary temperature of 1270°C. It should be mentioned here that the temperature in front of the orifice is not the same for the different scans. Therefore, the count rate at m = 28 (N_2, CO) strongly decreases because of the decreasing particle density when moving the spectrometer into the plasma jet, although there now must be a formation of CO.

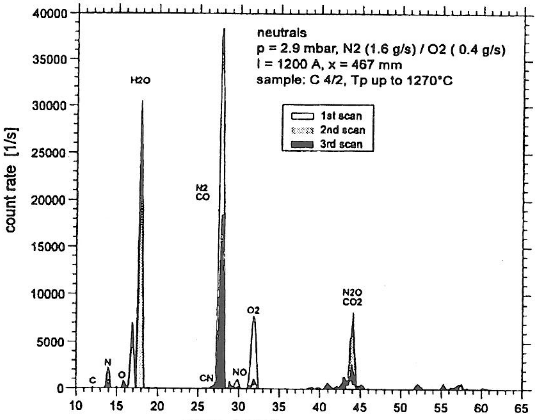

Fig. 2: Neutral particles in an N_2/O_2-plasma for a C-sample at different temperatures

As one can see the difficulty occurs that different particles may have such similar masses (here differences about 1/10 amu) that one does not succeed in separating the different species with a quadrupole mass analyzer. This is the case at the mass numbers 28 (N_2, CO) and 44 (CO_2, N_2O). If the sample is a SiC-sample, then also the species Si (m=28), SiO (44) and the similar masses SiC and Ar (40) may occur. Different methods have been applied to distinguish between these particles. The separation by the different ionization potentials can only be used if the potentials differ at least by 1-2 eV and if the counting rates are high enough, because the intensity of the signal rapidly decreases with decreasing energy of the ionizing electrons. With this method the presence of N_2 *and* CO in the 28-peak could be shown at the plasma conditions depicted in Fig. 2. The count rates also are too small for the identification of sufficient isotopes, the natural abundance of which usually is beyond 1 %. The specific cracking patterns which are generated by the electron impact dissociation provide more information. This method requires a calibration with the expected species. Although this approach is most suitable for large molecules with many fragments, it can be helpful in some cases in association with other methods.

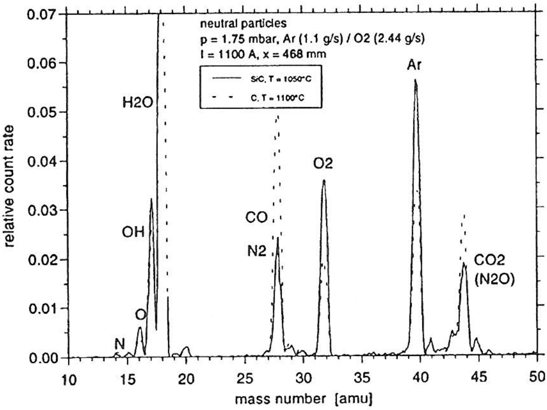

Fig. 3: Neutral particles in an Ar/O_2-plasma for different samples

	SiC-sample	C-sample
N_2, CO (m=28)	0.16	0.37
O_2 (m=32)	0.27	0.15
Ar (m=40)	0.43	0.27
CO_2 (m=44)	0.15	0.22
mean molecular weight	36.56	35.26

Table 1: Mole fractions of the main species

To minimize the number of different species, investigations were carried out in an Ar/O_2 plasma. In Fig. 3 a comparison of neutral particle mass spectra is shown between two tests at the same plasma conditions but with different samples, one C-sample at 1100°C and one SiC-sample at 1050°C. For the SiC-sample it can be assumed that at this temperature nearly no erosion occurs. The measured mass loss and investigations at the same plasma conditions support this assumption [6]. In this representation both spectra are standardized onto the total number of counts except the counts for H_2O (m=18) and OH (m=17), which are contained inside the mass spectrometer itself and can differ clearly for different tests depending on pumping time and quality of the high vacuum. The 28-peak in the SiC-scan consists of the N_2 of residual air in the mass spectrometer. Also, the 44-peak is only residual CO_2 inside the device. A similar amount is also contained in the C-scan. The difference of the count rates clearly shows, that, using the C-sample the oxygen reacts with the carbon to form CO as well as CO_2. This can be derived from the increasing peaks at the mass numbers 28 and 44 and the decreasing count rate at 32. At the same total pressure and temperature in front of the orifice the same total density of particles has to be there in both cases, the number of Ar-atoms has to decrease when more particles are formed by the reaction of one O_2-molecule to two CO-molecules. The values of the mean molecular weight and the mole fractions of the four main species CO, O_2, Ar and

CO_2 are listed in Table 1. This comparative method is also planned to be used to determine erosion products of SiC, accompanied by additional measurements carried out with a sample not producing CO and CO_2, e. g. glass.

CONCLUSIONS

The measurements show that the on-line-detection of erosion products behind a material sample is possible with the help of a mass spectrometer. By the identification of erosion products of graphite like CO and CO_2, it should be possible to detect the failure of protective coatings on C/C-materials. The erosion of SiC was not yet strong enough at the investigated plasma conditions to allow the reliable detection of erosion products. Further investigations have to be carried out to find the transition conditions between passive (i.e. formation of a protective SiO_2-layer) and active (formation of gaseous erosion products like SiO) oxidation behavior. In addition the influence of single plasma components on material samples has to be investigated because it may differ strongly depending on the gas mixture [7].

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