ENERGY TRANSFER AND OXYGEN ATOMS RECOMBINATION ON REFRACTORY MATERIALS. AGEING MECHANISMS OF THE MATERIAL

F. Nguyen-Xuan, S. Cavadias, J. Amouroux.
Laboratoire de Génie des Procédés Plasma -ENSCP- 11, rue P. et M. Curie
75231 Paris Cédex 05.

Abstract

In order to quantify the energy transfer from the reactive flow to a surface, the determination of recombination and accommodation coefficient is required. The following work concerns atomic oxygen flow recombining on metallic and silicon carbide surfaces, and finds its application in the study of space vehicles overheating when reentering the atmosphere. The recombination coefficient evaluation on metallic coatings enabled us to validate the actinometric method in a pulsed discharge. Then applied to the case of evolving catalycity of SiC material, over the 300-1023K temperature range, and coupled to surface analyses, this study can approach the understanding of the modifications, due to quick ageing, in this recombination process.

Introduction

This paper focuses on the recombination coefficient measurements, that quantifies the mass transfer, in so far as it corresponds to the number of recombining atoms over the number of atoms striking the surface. With respect to the quick ageing of the material, (modifications are supposed to occur during the first milliseconds of the exposition to the atomic flow), we used pulsed discharges of 400 milliseconds.

The first step is the recombination coefficient evaluation on electrolytically deposited metallic coatings, that present a large panel of catalycities. The axial atomic oxygen concentration profiles between the electrodes and the surface at the stagnation point, were obtained by. actinometry. In pulsed regime, with synchronization of the spectroscopic acquisition and the triggered discharge, the exposition time of the sample is perfectly monitored, and there is no thermal exchange between the plasma and the surface, during such short discharge times. Once the tests conditions were defined, we investigated material of great interest like SiC. The purpose is to clarify the evolving catalycity of this structure with the temperature, by coupling the recombination rate measurements in very short times, with XPS analyses. This study is indeed aimed at the understanding of differences in the catalytic behaviour in terms of surface chemical modifications, for predictions concerning reusable thermal protective systems.

The recombination coefficient "Gamma" determination in a pulsed plasma reactor.

During the very first seconds of the sample interaction with the plasma flow, modifications are supposed to occur, that would consequently influence the catalycity properties of the material. All experiments were then performed with the lowest exposure time, in order to follow the evolution of the material. Moreover, the pulsed regime allowed the sample to be free of the plasma / surface thermal exchange, and to control the exposure time to the plasma.

.Experimental set-up.

The experimental device includes a plasma tubular reactor, the controlling and acquisition apparatus(Figure 1).

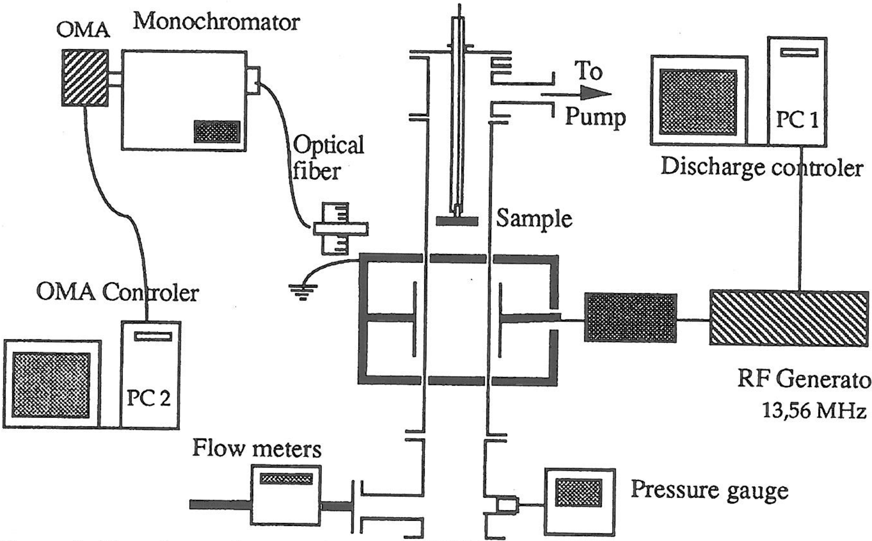

Figure 1: Experimental set-up for the recombination coefficient measurement in pulsed discharge. Test conditions: Air flow:230sccm/min, Ar:9.2sccm/min, Pressure: 2mbars, Power: 230Watts.

The low pressure tubular reactor used for "gamma" determination, was in vertical position for an easier sample arrangement. Tests were performed at 2 mbars pressure, and we use 230 ml/min flow for air gas, and 9,2 ml/min flow for Argon gas (about 4% of the total gas flow). The air plasma was created by a 13,56 MHz generator for short and very stable discharges. The emission spectroscopy signal was transmitted via an optical fiber, analyzed by a monochromator and detected by an Optical Multichannel Analyzer (O.M.A.). Including a photo-diode array and micro-plate intensifiers, the O.M.A. represents a flexible, quick and reliable way for signal acquisition. The spectral acquisitions are necessarily synchronized with the pulsed discharge. Using a discharge time of 400 ms, the total exposure time of the sample was 20 seconds, for one "Gamma" measurement.

The actinometric method applied to "gamma" measurement.

The recombination coefficients are calculated, using the spectroscopic method of actinometry. Actinometry involves the use of optical emission intensity ratios to provide an estimate of ground state species concentrations. The emission intensity from the species of interest is divided by the emission intensity from an inert gas (the actinometer) which is added to the plasma in small quantities. This normalization of the emission signal can correct for the fact that a change in emission intensity may be due to a change in excitation rate, resulting, for example, from a change in the electron energy distribution in the discharge, rather than from an actual change in species concentration. The following three conditions are sufficient to ensure that the emission intensity ratio X'/A' is proportional to the concentration ratio X/A, where X is the species of interest and A is the actinometer: 1) The excited species X' and A' must be produced by electron impact excitation of the ground state species; 2) The excited species must decay exclusively by photon emission; and 3) The electron impact excitation cross sections for X and A must have similar thresholds and shapes as a function of electron energy. In practice, it may be possible for X'/A' to be proportional to X/A over some range of plasma conditions even if all three conditions are violated. In our case the O atom concentration has been monitored with optical emission from O(844.6 nm) Ar(750.4 nm). The ratio IO/IAr obtained by actinometry is related to the concentrations ratio by the following relation:

$$IO / IAr = k\,(O) / (Ar),$$

and it can be used as a tracer for atomic oxygen concentration.

The "Gamma" coefficient evaluation on metallic coatings

The samples

The samples investigated are electronically deposited metallic coatings, presenting a large panel of catalycities: copper, silver, gold, zinc and stainless steel should have different orders of magnitude for the recombination coefficient of the atomic oxygen.

Results

The "gamma" coefficient quantifies the mass transfer, in so far as it corresponds to the number of recombining atoms over the number of atoms striking the surface. Measurements are performed near the surface at stagnation point, in the boundary layer, where movement of species is purely diffusive. The atomic oxygen concentration evolution is also described by diffusion equation, and we can observe a linear decreasing oxygen concentration due to the atoms recombination. After the boundary layer characterization, with the determination of the diffusional slope P and the thickness of the boundary layer L, the value of γ is given by:

$$\gamma = (-P*4*D) / c * (-P*L + (IO/IAr)_0)$$

where D: Binary diffusion coefficient (cm^2/s) c: species velocity (m/s), and $(IO/IAr)_0$ initial concentration

In fact, during the very first seconds of the sample interaction with the plasma flow, modifications are supposed to occur, that would consequently influence the catalycity properties of the material. All experiments were then performed with the lowest exposure time, in order to follow the evolution of the material. Moreover, the pulsed regime allowed for the sample to be free of the plasma / surface thermal exchange, and a control of the exposure time to the plasma. Parameters like the initial atomic oxygen concentration and the thickness of the boundary layer are obviously independent of the sample nature, and should be constant from one measurement to another. We also have to know the binary diffusion coefficient D=200 cm^2/s, the atomic velocity c=628 m/s, the thickness of the boundary layer L=10 mm. Our results agree with previous literature (Table 1).

METAL	Gamma (Our measurements)	Gamma (References)
Silver	10^{-1} + 30%	$2,4.10^{-1}$ [3]
Copper	$1,5.10^{-1}$ + 20%	8.10^{-2} [2]
Gold	$7,5.10^{-3}$ + 20%	8.10^{-3} [2]
Zinc	$5,5.10^{-3}$ + 20%	
Stainless steel	$4,6.10^{-3}$ + 20%	$9,9.10^{-3}$ [1]

Table 1: Comparison of our recombination coefficient values to the literature's ones.
(Pressure=2mbars, Power=200Watts, Discharge time=400ms, Air=230sccm/minn, Argon=9,2 sccm/min)

Insofar as the materials are not precisely characterized in the literature's results, the differences observed, can be attributed to differences in the coating process, or in the alloy composition, as with the stainless steel, for instance. This experimental set-up gives Gamma coefficient values with a precision of about 30%, which is acceptable. We can thus conclude that the actinometry method in pulsed regime is reliable, and that the reproducibility of the experiments is satisfactory.

As a conclusion, the large panel of catalycity values we obtained enabled us to validate in a significant way our "gamma" determination. We can then quickly classify materials according to their susceptibility for oxygen recombination.

Finally, by controlling the exposure time, this experimental set-up can provide "gamma" measurements with respect to the ageing time of the material. This experiment will be able to approach the catalycity behavior differences in relation with surface modifications.

The evolution of the structure with the surface temperature.

"Gamma" measurements as a function of the temperature

The recombination coefficient measurements were performed also in silicon carbide samples, using the same experimental set-up, at several temperatures ranging between 300 and 1000k. The "gamma" values lie between 0.004 and 0.013, presenting a linear increase till 900K where the curve shows a break of the slope due to the change of the mechanism of the recombination reaction (Figure 2).

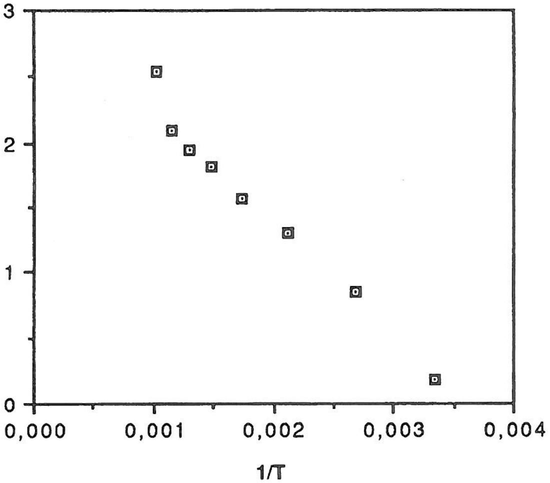

Figure 2: Evolution of the "Gamma" coefficient with increasing temperature.
(Pressure 1mbar, power: 250Watts, Gas flow: 260sccm/min, Discharge time: 2s.)

These experiments were coupled to chemical surface analyses in order to understand the catalytic behavior evolution in relation with surface chemically evolving.

Following the quick ageing of SiC surfaces by ESCA analyses.

The plasma-surface interaction, and particularly, the specific surface recombination reaction of the atomic oxygen, depends strongly on the chemical state of the surface material. In fact, the reactive flow interaction should be different if the material is already oxidized or not. Moreover, this surface "passivation" can occur in the very first milliseconds of the discharge.

Principle of the analysis: This non destructive analysis gives qualitative and quantitative information about surface species. The ESCA. spectroscopy is based on the photoelectric effect. Samples are irradiated with X rays (1500 eV), and the kinetic energy of the ejected photoelectron enabled us to determine the bond energy between the electron and the atom, taking the surrounding electrons into account. The electronic energies are calculated with a precision of about 0,1eV, and the thickness of the analyzed layer is 60 Å. We designed five types of sample: all samples were exposed for 140 seconds to the reactive flow of atomic oxygen, and each was heated, about two hours, at four different temperatures: 100°C, 200°C, 300°C, 440°C. As expected, the oxygen peak increased with the temperature, according to the catalycity evolution described above. Figure 3 compares the silicon carbon bond and the silicon oxygen bond peaks for the non treated sample and for the highest temperature sample (715 K).

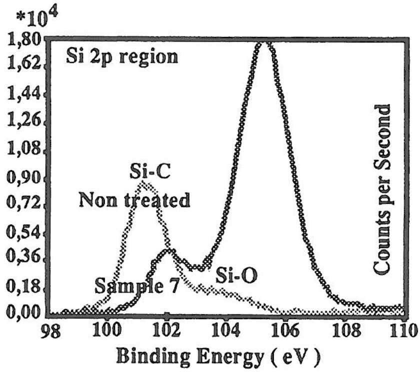

Figure 3: XPS analysis comparison between the silicon carbon bond and the silicon oxygen bond peaks for a non treated sample and the temperature sample (715 K) 1,1 mbars-250 W--260 ml/min- discharge time=2 sec-

This shows the progressive evolution of the SiC structure towards an oxidized silicon structure, which is in total agreement with the increasing quantity of recombining oxygen atoms. As expected above, the Gamma coefficient is increasing with the sample temperature. ESCA analyses allow us to conclude that even in such a short time (140 seconds), and with low temperature differences, chemical surface modifications occur already.

Conclusion

The first part of this work consisted in validating the actinometric method applied to "Gamma" coefficient determination in pulsed discharges. The different metals investigated gave reproducible results in good agreement with the literature. But the interest of the study is to correlate the evolving catalycity of refractory materials like silicon carbide, with their chemical surface modifications. Moreover, the use of the pulsed reactor in the experiment avoid thermal exchange between plasma and surface due to the short discharge time. The ESCA analyses show a clear evolution of the SiC structure towards a quartz structure in very soft experimental conditions, justifying the interest in pulsed discharge measurements. Further experiments should give information about the recombination mechanisms, occurring at high temperature or in aged materials.

Acknowledgments

This work was financially supported by CNES and ESA under Dassault Aviation contract.

References

[1] Wickramanayaka, S., Meikle, S.,: J. Vac. Sci. Technol., 1991, A9, 2999.
[2] K. Nakada,. Bull. Chem. Soc. Japan, 32, 809, p-1072, 1959.
[3] G.A. Melin, R. J. Madix, Trans. Far. Soc., 67, p-198, 1971.