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Dissociation of CO_2 molecules in microwave plasma

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ABSTRACT

Dissociation fraction of CO_2 molecules was measured in an early afterglow of microwave plasma by catalytic probes. The experiments were performed using the MESOX facility at the focus of the 5 kW solar furnace of PROMES-CNRS. Plasma was created in a quartz tube within a microwave cavity powered with a generator with adjustable power between 200 and 1200 W and frequency of 2450 MHz. The dissociation fraction was measured by catalytic probes at different flows of carbon dioxide gas up to 20 l h^{-1} corresponding to different pressures up to 150 Pa. The dissociation fraction reached 13% at the pressure of about 20 Pa. The density of O atoms at the probe position was increasing with discharge power and was almost 10^{21} m^{-3} at the highest power. A broad maximum in the O-atom density versus pressure was observed. The results were explained by gas-phase and surface reactions.

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1. Introduction

The European Space Agency (ESA) plans missions to Mars and Venus in the frame of the Cosmic Vision 2015-2025 program [1]. The space vehicles will be exposed to extreme conditions at the entrance of the atmosphere which is mainly composed of carbon dioxide (more than 95%) and some nitrogen (few percent) with traces of some other gases. The pressure in the Mars atmosphere of course depends on the altitude and is between 30 Pa on the highest mountain Olympus Mons's peak and 1155 Pa in the depths of the deepest crater Hellas Planitia. In order to prepare suitable materials for the outer shield of the space vehicles, the interaction between carbon dioxide and the possible materials should be elaborated in advance. Due to the high velocity of the space vehicles at the entry of the atmosphere, carbon dioxide will be transformed to the state of plasma. Interaction of plasma particles with solid materials is completely different from the interaction of parent molecules. Carbon dioxide is dissociated and ionized in the plasma. The major dissociation product is atomic oxygen which is chemically extremely reactive and readily interacts with solid materials. Recent studies on the interaction of various materials with O-rich plasma showed that not only the surface composition but the morphology is changed significantly even at short exposure to plasma at elevated temperatures [2]. In order to predict the behavior of the materials at the entry of space vehicles to the Mars or Venus atmospheres, extensive studies on the treatment of suitable materials with carbon dioxide plasma at elevated temperatures should be performed on Earth. Most experiments were performed in special high-frequency plasma reactors producing subsonic flow of carbon dioxide while some experiments were also performed in microwave (MW) plasma reactor as in our case [3–5]. Sepka et al. [5] have used MW source and experiments were performed in the side-arm diffusion tube which was used to study surface catalycity according to Smith diffusion method (sink of reactant species on the tube walls as a function of axial location along the side-arm tube). In our case experiments are foreseen at the European solar facilities in Font-Romeu, France, where a suitable plasma reactor was built. In this laboratory reactor, similar plasma can be created as it is formed in the shock wave and in the diffusion boundary layer in front of the space vehicle i.e. high dissociation rate of carbon dioxide and low ionization rate at similar pressures as in Mars. The plasma reactor was designed for studying catalytic reactions on material surfaces. It is placed at the focus of the 5 kW solar furnace that enables heating of the samples and due to a variable opening shutter, a precise control of the temperature up to 2500 K is obtained. Such equipment allows studying the surface oxidation, erosion and ablation of thermal protection system of space vehicles. Before performing any experiments with samples, the characteristics of carbon dioxide plasma should be elaborated. Since the major reactants in the plasma are neutral O atoms (rather than charged particles), the major plasma parameter is the dissociation fraction of the CO_2 molecules.

2. Experimental

The experimental system is shown schematically in Fig. 1. The experimental chamber is a quartz tube with the outer diameter of 54 mm and the inner diameter of 50 mm. On one side, carbon dioxide is introduced through a calibrated flow controller while

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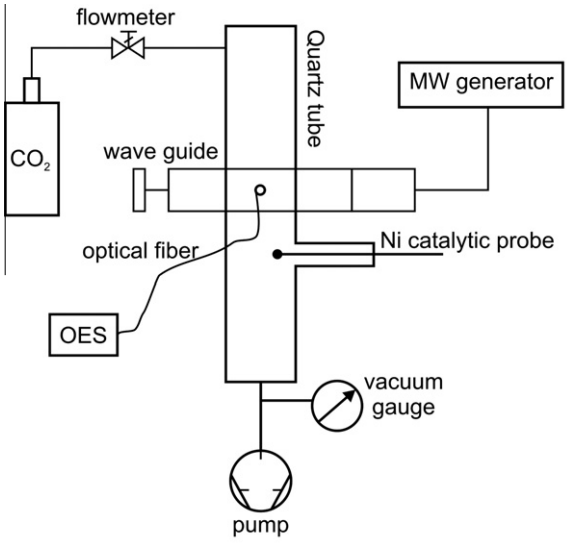

Fig. 1. Experimental set-up.

on the other side it is pumped with a two stage rotary pump with the nominal pumping speed of 28 $m^3\,h^{-1}$. The gas entering the experimental chamber passes a microwave cavity where plasma is created by a microwave generator. The power of the generator is adjustable up to 1200 W, while the frequency is constant at 2450 MHz. At current experiments, power up to 700 W only was used.

A catalytic probe for measuring the dissociation fraction is mounted 20 cm away from the discharge cavity as shown in Fig. 1. The probe was not mounted in the cavity (plasma) itself due to the unwanted interaction with the electromagnetic field in the cavity as well as due to exothermic neutralization of the charged particles. Namely, any attempt of mounting the probe close to the cavity resulted in the probe melting. The probe was a standard fiber optic nickel catalytic probe shown in Fig. 2. The details of the probe construction were published first by Babic et al. [6]. The probes performed excellent at experiments where they were compared with another standard method for determination of the neutral oxygen atom density – chemical titration using NO gas [7]. Furthermore, comparison of the catalytic probes with another method for quantitative determination of the atom density in the plasma afterglow, TALIF (Two-Photon Absorption Laser Induced Fluorescence) [8], showed extremely good agreement. The absolute accuracy of the probes was estimated to be similar to other methods – about 30% [9].

The principle of probe operation is rather simple. When a catalyst is immersed into radical rich atmosphere, extensive heterogeneous surface recombination of radicals takes place. The consequence of recombination is heating of the catalyst material. In fiber-optic probes the catalyst material is wrapped around a small sphere. The sphere is an integral part of an optical fiber. A catalytic material is heated to a pretty high temperature and emits infrared radiation as a grey body. The radiation is focused by the sphere and enters the optical fiber. The optical fiber is connected to an appropriate infrared detector on the other side. The detector is a Ga–As crystal that is sensitive to infrared radiation. The sensitivity decreases with increasing wavelength so the detection limit is often around 400 K. This value of course depends slightly on the type of the material emitting infrared radiation. The upper limit of the detector is defined by the saturated current and is at the temperature of about 1000 K. By replacing the Ga–As detector with a standard silicon one the upper limit can be increased to much higher temperatures but in practice no advantage is gained due to the fact the catalyst material does not stand heating to very high temperatures. Also, silicon detectors have poor sensitivity in the far infrared range i.e. at low temperatures. A handful of materials express pretty good catalytic activity for recombination of neutral radicals. In practice, however most materials have important drawbacks such as temperature dependent recombination coefficient or even discontinuity in the recombination coefficient. These drawbacks limit the choice of materials. Numerous studies have shown that nickel is a pretty good choice as long as the major radicals are neutral oxygen atoms.

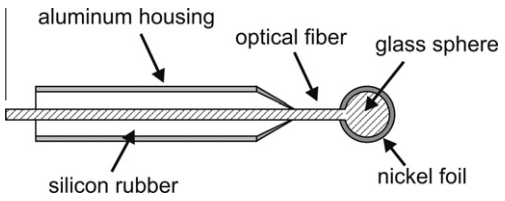

Fig. 2. Schematic of the catalytic probe.

The temperature limit also defines the range of radical density where the probe works. Obviously, the probe does not operate well at very low density of radicals, and melts at very high density of radicals. The probe temperature depends on heating and cooling rates. The heating rate obviously depends only on the density of radicals in the vicinity of the catalyst and the recombination coefficient, while cooling depends on physical properties of the probe, gas pressure, as well as the density of radicals in the vicinity of the probe. At very high density of radicals, the probe is heated to temperatures close to/or exceeding 1000 K so cooling by radiation prevails. In such a case the detection limit obviously does not depend on pressure. On the other hand, when the density of radicals is not high enough to assure that high temperature, the sensitivity depends on pressure. Obviously, the parameter that influences the lower detection limit is the dissociation fraction. The density of radicals is measurable down to the value of several $10^{19}\,m^{-3}$ providing the pressure is low (the dissociation fraction is high). The lower detection limit therefore cannot be given as a fixed value. If the dissociation fraction is low so that the temperature of the catalyst does not increase over the detection limit of the probe, standard thermocouple probes are a better choice [10]. Here, it is worth mentioning that standard thermocouple probes often do not work in high-frequency discharges due to the interference effects caused by the field. The immunity of fiber optics catalytic probes to electromagnetic interferences is actually the major advantage of such probes.

The dissociation fraction was therefore measured 20 cm away from the plasma region downstream the gas flow. Taking into account the pumping speed and the inner diameter of the quartz tube the average drift velocity of gas particles in the tube is

$$v_D = V_p/S \tag{1}$$

where V_p is the pumping speed of the rotary pump and S is the cross section of the tube. Taking into account the numerical values the average drift velocity is 4.0 $m\,s^{-1}$. The time that particles need to transverse the path between plasma and the probe is therefore 50 ms.

Plasma was characterized also by optical emission spectroscopy. There are two narrow gaps in the waveguide that allow for plasma monitoring by optical emission spectroscopy. An optical fiber which transfers the optical radiation from plasma to an optical spectrometer is placed in the gap in the waveguide. Emission spectra were recorded using an AVANTES AvaSpec 3648 spectrometer. Spectra were measured in the range from 200 to 1100 nm. The

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