Experimental and Numerical Modelling of Heterogeneous Recombination for Martian Entry Conditions

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Reliable knowledge of probe entry environment is one of key features to achieve success of future Mars missions. This environment strongly depends on Mars entry scenario but also extensively on the thermo-chemical model of Martian atmosphere. Though much work in development of relevant thermochemical model of high-speed/high-enthalpy flows of carbon dioxide (main constituent of the Mars atmosphere) has been done at the moment throughout the world the actual experimental data for hightemperature conditions remain rather scarce and rates of many nonequillibrium processes is known with high degree of uncertainty (of order of magnitude and even greater). Thus any new experimental data obtained in high-enthalpy conditions will contribute to the improvement of existing chemical and physical models for such kind of flows. In particular, this also concerns the rates of heterogeneos chemical processes at a vehicle sutface. Since in nonequilibrium flow conditions use of lowcatalytic thermal protection materials can multiply reduce the heating rate of the vehicle surface compared to highcatalytic materials then the problem of surface catalysis specification turns to be very important for ensuring required thermal state of the entry porbe at the lowest TPS weights.

A number of new experimental data were obtained during test campaign in high-enthalpy inductively coupled plasmatron facility U-13 of TsNIImash (Russia) within the frameworks of EU FP7 SACOMAR project (Key Technologies for Safe and Controlled Martian Entry). To study hightemperature Mars atmosphere plasma (was modeled with CO_2(97%)+N_2(3%) mixture) interaction with different surface materials the tests were carried out for three test samples with different surface catalycities (relative to recombination probabilities of CO_2 plasma species): silver (material assumed to be the most catalytic among others), quartz (low-catalycity material) and copper (is known to be high catalycity material for air plasma and to be of intermediate catalycity for Martian atmosphere gases) for two flow enthalpies – 9 and 13.8 MJ/kg and several reference values of Pitot pressure from 10 to 80 hPa. These test parameters corresponds to stagnation conditions for two high-altitude points of shallow (stormy) trajectory of future EXOMARS probe.

Presented paper addresses the results of flow diagnostics in U13 ICP facility as well as test results on the catalytic properties of studied surface materials in high-enthalpy carbon dioxide flow obtained during the experimental campaign. Also, these experiments were rebuilt by means of CFD modelling of test conditions that includes solution of combined Maxwell – Navier-Stokes equations for nonequillibrium gas mixture in the facility inductor and Navier-Stokes equations for flow around the test model within the work section of the facility. The surface catalysis model includes three general processes: (i) surface absoption/desorption of atomic oxygen, (ii) oxygen heterogeneous recombination following to the Eley-Rideal mechanism and (iii) CO molecule surface recombination through the Eley-Rideal mechanism.

Compared to more ususal case of air species surface recombination at the Earth atmosphere entry conditions the dissociated CO2 flow surface recombination for Mars entry environment has some specific traits. In particular (neglecting low value of atomic nitrogen), atoms of surface adsorbed oxygen may competitively react with either inflow atomic oxygen or carbon monoxide that does not take place for dissociated air where adsorbed oxygen and nitrogen atoms may form only corresponding molecules. This circumstance make difficult using single “effective” constsnt of surface catalycity for nonequilibrium dissociated flow of carbon dioxide, and surface reaction rates (at least principall ones) should be studied instead.

Results of CFD modelling demonstrated that electrolysis coated silver (used in tests) cannot be referred to as fully catalytic material for CO_2+N_2 mixture species recombination for the test conditions and the most appropriate recombination probabilities for that material can be accepted to be $\gamma_O = 0.01$ and $\gamma_{CO} = 0$. Just the same values of heterogeneous recombination probabilities can be admitted for copper surface.

Comparison of numerical and experimental data shows that the quartz surface turns to be of low but nevertheless finite catalycity. It may be concluded that recombination probabilities for quartz surface in dissociated CO_2 flow are $\gamma_O \approx \gamma_{CO} \leq 10^{-3}$.

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