

Investigation of Nonequilibrium Heat Exchange and Catalytic Properties

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Abstract

The methodology of investigation of nonequilibrium heat exchange and catalytic properties is given. The high temperature experiments were conducted at wind-tunnel VAT-104 of TsAGI. This facility gives opportunity to simulate conditions of flight with velocities 3-8 km/s at altitudes of 60-100 km. The data on catalytic properties of some materials and information on values of heat flux to samples with different catalytical activity are presented. It is shown that impact of the high-speed plasma flow on ceramic sample results in sample temperature leap of some 1000 K. The gain in specific heat flux up to threefold is coursed by catalyticity tenfold increase. The temperature and heat flux leaps are due to formation of high-catalytic thermal barrier HfO₂ film. The temperature difference over thermal barrier film is up to 1500 K, film thickness being near 0.5 mm.

Keywords: heat flux, atoms heterogeneous recombination.

Nomenclature

The heat flux exchange of high-speed vehicle (HSV) at a number of regimes is nonequilibrium, the main contribution into the heat flux being a heat of atom recombination. In the strong bow shock wave almost full dissociation of air molecules take place. The recombination of atoms into molecules at the vehicle surface may lead to considerable gain in the heat flux (up to four times). The examination of catalytic properties is aimed at the sufficient decreasing of heat flux due to using of the newly created materials with low catalytic activity.

The impact of the high-speed plasma flow gives rise to a number of physical – chemical processes. So the plasma flow – surface interaction should be studied. The investigations were performed in a VAT-104 wind-tunnel, making it possible to simulate the conditions of HSV flight [1]. VАТ-104 is equipped with a high frequency induction gas heater providing high stagnation temperature up to 10000 K without contamination. Flow velocity is 4-5 km/s, Mach number $M=4-8$, heat flux Q=0.1-10 MW/m². The VAT-104 wind-tunnel provides reproducible and repeatable regimes (>97%), test duration up to 0.5 h and long total service life $(10^4$ h). These characteristics are especially important in investigation of nonequilibrium heat exchange and material catalytic proper-ties.

The specific heat flux and nonequilibrium component of the heat flux are determined. The tests are accompanied with numerical simulation of the overflow and heat exchange [2-4]. The code for numerical simulation of a gas heating in the induction heater, and the codes for calculation of the flow in a Laval nozzle and in an under-expanded jet [5] are fitted up for calculations of processes in

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VАТ-104. The technology used is based on the complex of programs for numerical integration of Navier-Stokes equations and special program-generators, which interact with the data bases on gas thermodynamic and transfer properties [6]. The computer code involves eleven-component model of air medium. Thermal diffusion and eradiation are neglected.

A number of designs of supporting devices were used, which enable a thermal insulation of a sample to be obtained. A heat flux to a sample is determined using brightness temperature distribution over the sample. The brightness temperature is measured with a pyrometer based on a VS-CTT-285/E/P-2001 digital CCD camera at a wave-length of 890 nm [7] and a Tandem VS-415U thermal imager at 650 nm. The pyrometer and thermal imager are calibrated with a standard black body. Emissivity of a sample is obtained from sample thermal spectrum, measured with spectrometer Ocean Optics USB2000+ [8]. The spectral temperature and spectral emissivity of a sample are determined at wavelengths of 650, 801 and 890 nm. The values of emissivity and brightness temperature allow the sample temperature to be found. All parameters of the tests are recorded on the PC.

The flow in VАТ-104 is nonequilibrium. The degree of dissociation and vibration temperatures are «frozen» near the nozzle critical section. The specific heat flux depends on material catalyticity. Measured values of the specific heat flux to a copper calorimeter, to molybdenum disk coved with MAI D5 coating [9] and to disks of super-high temperature ceramics are presented on Fig. 1. The specific heat flux is seen to be depending on catalytic activity of the model investigated.

Fig 1. The specific heat flux to some models

The effective rate constant of air atoms heterogeneous recombination K_w was determined using the known value of K_{ws} for the reference sample, the experimentally measured difference in the specific heat fluxes ΔQw, to the examined and reference samples and derivative dKw/dQ^w from the relationship:

$$
K_w = K_{ws} + \frac{dKw}{dQw} \cdot \Delta Q_w. \tag{1}
$$

The derivative dK_w/dQ_w is calculated using derivative dK_w/dT_w which was obtained in the parametric numerical simulation of the overflow and heat transfer of the model [3]. The errors in determining of a material catalyticity are associated with uncertainties in a specific heat flux measurement. The measures are taken to eliminate methodology errors. As reference samples disks coved with thoroughly studied [9] MAI D5 coating were used in most cases. Both reference and examined samples are thermally insulated and tested in identical conditions.

In most cases a tested model is supported with corundum rods to be thermally insulated. For sample thermal insulation at supreme high temperatures tests it is supported with a thin rod of boron carbonitride. A specific heat flux to a sample is determined using brightness temperature distribution over the sample.

While investigating plasma flow – surface interaction at supreme high temperatures [10] a number of interesting effects are found (Fig. 2). The tested samples were disks of super-high temperature ceramics, based upon hafnium diboride HfB₂ ore zirconium diboride ZrB₂.

Fig 2. Parameters of a typical test of a ceramics sample: stagnation pressure P_0 ; anode power of gas heater Wa; temperature of the disk front T_f and backside T_b surface, K

At stationary regime of heating of a disk the brightness temperature of its front surface increases abruptly to over 1000 K. This effect is associated with formation of thermal barrier film of HfO₂, which has high catalytic activity. At the sample temperature of approximately 2000 K there is a rapid loss of silicon dioxide SiO₂, which leads to a sharp increase in the surface catalytic activity. A sharp increase of surface catalyticity results in high-rate rise in the heat flux and, consequently, temperature. Due to formation of a highly catalytic film, the heat flux to the sample increased threefold and amounted to Q≈300 W/cm². The effective rate constant of air atoms heterogeneous recombination K_w rose tenfold to 22 m/s, the rate constant being determined from Eq. 1. The high catalytic activity of a thermal barrier film is apparently caused by air atoms incorporation into the crystal lattice of hafnium oxides with the following recombination in it. The recombination energy is fully transferred to the surface. Note that at such a high temperature about 3000 K the sample surface is completely free from adsorbed atoms, so recombination processes according to the Eley-Rideal and Langmuir-Hinshelwood mechanisms become inefficient.

The temperature gradient over thermal barrier film is some 1500 K, film thickness being 0.5 mm. The heat flux to the sample is almost fully irradiated. The formation of such a thermal barrier film, for instance, at a wall of a burning camera will be very useful and permits to increase the efficiency of a jet engine.

Fig 3. The distribution of calculated heat flux over a disk

The experiments are accompanied with numerical simulation. On Fig. 3 the data of calculation of heat flux to a disk of super-high temperature ceramics are shown. The disk diameter and thickness are 20.85 mm and 5.45 mm, correspondingly. The calculation was made for conditions of experiment: stagnation pressure 45 kPa; anode power of gas heater 218 kW; air discharge 3.3 g/s; working chamber pressure 307 Pa; distance from nozzle exit 75 mm; rate constant of air atoms

heterogeneous recombination is taken 30m/s and 3m/s for the disk front and back sides, correspondingly. The calculated and measured total heat flux is, correspondingly, 971.4 and 1092 W.

On Fig. 4 a photo of test of a thin wedge of super-high temperature ceramics at zero angle of attack is shown. The radius of wedge edge is 0.5 mm. Due to big enough thermal conductivity of ceramics, the edge sustained a big specific heat flux of \sim 250 W/cm², the edge temperature being only 1650 K.

Fig 4. A photo of test of a thin wedge

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