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Quantum mechanics calculation of catalytic properties of a copper sensor for prediction of flow characteristics in plasmatron

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ABSTRACT

Basing on quantum-mechanical calculations within cluster models, rate coefficients of elementary steps of the complete system of heterogeneous catalytic recombination of dissociated oxygen on the copper oxide surface were determined. They were used for calculation of dependence of the effective coefficient of oxygen atom heterogeneous catalytic recombination on the temperature and partial pressure in a wide range of conditions at the surface. It has been established that its value substantially varies depending on the conditions at the surface.

1. Introduction

The great practical interest to the study of interaction between multicomponent gas mixtures and catalytic thermal barriers is connected with creation of reusable spacecrafts and promising hypersonic aircrafts. Such space/aircraft experience non-equilibrium flow conditions in high-heat parts of the flight path in the atmosphere, and application of low-catalytic coatings reduces heating several times due to heterogeneous catalytic atom recombination. Considerable reduction of heat flows allows reducing the thermal protection weight and increasing the payload [1–3].

High-frequency induction plasmatrones are efficient experimental facilities for studying thermal barrier catalytic properties [4]. Metal (often copper) sensors are used in them for the purpose of flow diagnostics [5]. The flow parameter values to be determined to a great extent depend on the sensor material catalytic activity degree.

At mathematical problem setting the catalytic activity of the surface is included into the boundary condition for a set of equations describing the multicomponent chemically reacting flow at the surface. Heterogeneous catalytic recombination effects are normally considered by introduction of recombination coefficients γ_i showing the share of atoms recombining on the surface. Coefficients γ_i depend both on the surface properties, and the gaseous phase conditions. These dependences include many parameters.

Rather a detailed review of the results of experiments that consisted in measuring the possibility of heterogeneous recombination of oxygen atoms γ_O on copper and its oxides is given in paper [6]. In $300 \div 600$ K surface temperature range a high level of oxygen atom heterogeneous recombination possibility ($\gamma_O \approx 0.1 \div 0.5$) on CuO and Cu_2O surfaces is observed, and the values for Cu_2O are somewhat exceed the values for CuO.

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Providing the appropriate selection of elementary step rate coefficients, theoretical models accounting for a detailed mechanism of heterogeneous catalytic reactions and based on Langmuir adsorption layer theory [7], allow satisfactory description of aerodynamic heating both the windward surface of reusable spacecrafts along their entire descending trajectory in the Earth atmosphere, and models in experimental facilities [1,3,8,9]. But the mentioned coefficients have a number of parameters determined when compared with heat flow experimental data, and this approach can be ambiguous ambiguous in case with multiparameter dependence [10].

Approaches based on quantum mechanics and molecular dynamics methods allow better understanding of heterogeneous catalytic process mechanism and determination of elementary step rate coefficients without using experimental data. Papers, [11,12] in accordance with classical molecular dynamics principles contain calculations of coefficients of oxygen atom recombination and recombination energy accommodation on siliconized thermal barrier coatings (β-cristabolite and SiC) using oxygen and material atom interaction potentials known from prior art., [13,14] describe the study of oxygen atom heterogeneous recombination on aluminum oxide surface using the semiclassical approach. This approach implies the application of quantum mechanics methods based on DFT [15] to determine the potential energy surface complying with O (^{3}P) atom interaction with the cluster modeling the α-Al_2O_3 surface, which is then used in molecular mechanics calculations. Papers, [16,17] describes the study of dissociated air interaction with thermal barrier ceramic coatings (β-cristabolite (111) and α-Al_2O_3) based on quantum-mechanical calculations and the transition state theory.

In this paper the cluster approach is applied to dissociated oxygen interaction with Cu_2O copper oxide surface. Using quantum mechanics methods geometric, energy and vibrational properties of oxygen atom heterogeneous recombination are calculated. The Schrodinger equation in adiabatic approximation was solved by application of the density functional theory (DFT) methods using the GAUSSIAN software package. The elementary step rate coefficients were calculated depending on the temperature basing on the transition state theory of Eyring and Polanyi. The above was the basis for determination of γ_O recombination coefficient values in a wide range of conditions change at the surface. The obtained results are consistent with the experimental data.

2. Modeling recombination processes and structure of material surface

When copper sensors are used as parts of a high-frequency induction plasmatrones in dissociated air, cuprous oxide Cu_2O is produced on their surface. This is a red–brown crystalline substance. Its crystalline structure can be represented as a body-centered cubic lattice with oxygen atoms in the nodes, and an interpenetrating face-centered lattice of the same size but with copper in nodes, one quarter-shifted along the body diagonal. Copper coordination is equal to two, oxygen coordination—to four. Cell dimension a_0=4.26 Å. The melting point is 1236 °C, the break-down temperature is 1800 °C (the highest among all copper oxides).

Both the impact and the associative mechanisms of heterogeneous recombination were taken into account on Cu_2O surface, and the rate coefficients of the respective elementary steps were calculated

oxygen atom adsorption/desorption

$$O+(S)\overset{k_a,k_d}{\leftrightarrow}(O-S)$$

Eley–Riedel (ER) mechanism of recombination (impact recombination)

$$O+(O-S)\overset{k_{er}}{\rightarrow}O_2+(S)$$

Langmuir–Hinshelwood (LH) mechanism of recombination (associative recombination)

$$(O-S)+(O-S)\overset{k_{lh}}{\rightarrow}O_2+2(S)$$

Here (S), (O–S) are symbols of free adsorption sites and adsorbed oxygen atoms.

Since chemisorbed particles bound to the surface by short-range forces are involved into heterogeneous catalytic reactions on the surface, the cluster approach is rather efficient for description of local interactions. A cluster is a relatively small part of a solid body lattice consisting of a finite number of surface and near-surface layer atoms. The study of interactions with it reveals the possibility of direct application in the calculations of quantum mechanics methods dealing with molecular systems limited in terms of size.

The Cu_2O copper oxide surface was modeled by three near-surface layers (Fig. 1), determining clusters Cu_2O_5, Cu_4O_8 and Cu_5O_8 (Fig. 2). The first cluster was used for calculation of atomic oxygen adsorption/desorption adsorption/desorption and impact recombination processes,

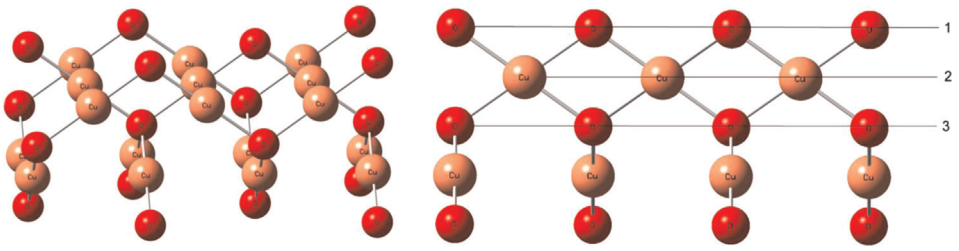

Fig. 1. Cu_2O copper oxide crystal structure (on the left) and side view (on the right).