A new surface catalytic model for silica-based thermal protection material for hypersonic vehicles

Li Kai, Liu Jun, Liu Weiqiang [*]

Science and Technology on Scramjet Laboratory, National University of Defense Technology, Changsha 410073, China

Abstract   Silica-based materials are widely employed in the thermal protection system for hypersonic vehicles, and the investigation of their catalytic characteristics is crucially important for accurate aerothermal heating prediction. By analyzing the disadvantages of Norman's high and low temperature models, this paper combines the two models and proposes an eight-reaction combined surface catalytic model to describe the catalysis between oxygen and silica surface. Given proper evaluation of the parameters according to many references, the recombination coefficient obtained shows good agreement with experimental data. The catalytic mechanisms between oxygen and silica surface are then analyzed. Results show that with the increase of the wall temperature, the dominant reaction contributing to catalytic coefficient varies from Langmuir–Hinshelwood (LH) recombination ($T_W < 620$ K) to Eley–Rideal (ER) replacement (620 K $< T_W <$ 1350 K), and then to O_2 desorption ($T_W > 1350$ K). The surface coverage of chemisorption areas varies evidently with the dominant reactions in the high temperature (HT) range, while the surface coverage of physisorption areas varies within quite low temperature (LT) range ($T_W < 250$ K). Recommended evaluation of partial parameters is also given.

1. Introduction

Recently, more and more attention has been drawn to the research on hypersonic vehicles.[1] As such vehicles are required

to withstand severe heat loads, accurate characterization of the aerothermal heating of such vehicles is essential to their design.[2,3] One significant contribution to the heating comes from the chemical recombination reactions occurring on the surface of the vehicle, namely diffuse heat. It has been proved by a mass of numerical and experimental results[4–6] that the surface catalytic condition has a significant impact on this heat flux prediction, and a reasonable surface catalytic model is rather meaningful to the accurate simulation of the heat flux.

At present, the finite-rate catalytic model (FRSC) can be divided into three groups: specified reaction efficiency (SRE) model, FRSC model and combined surface catalycity (CSC) model.

[*] Corresponding author. Tel.: +86 731 84574177.
 E-mail addresses: LiKai898989@126.com, likai89@nudt.edu.cn (K. Li), Liujun19711019@sina.cn (J. Liu), liuweiqiang_1103@163.com (W. Liu).
Peer review under responsibility of Editorial Committee of CJA.

The SRE model is based on the catalytic efficiency, and is also called catalycity model. In this model, γ_s is temperature-dependent, and is often assumed to be in the form of Arrhenius formula such as Scott model, Zoby model, Gupta model,[7] etc. FRSC model is based on non-equilibrium catalytic reactions. In this model, the heterogeneous catalytic reactions are coupled into the homogeneous gas reactions, and the reaction rate k_s is calculated directly by solving the non-equilibrium equations. Representative models are Park's model,[8] and Marschall and MacLean's model.[9]

Considering the excessive dependence on the parameters from the experimental data of SRE model and the large calculation scale of FRSC model, a combined surface catalysis model, namely CSC model, has been proposed. Like the SRE model, the recombination rate is still assumed to be the product of the catalytic efficiency γ_s and the kinetic velocity of impinging gas particles. However, a plenty of gas and solid surface interactions are considered for the modeling of the recombination coefficient, including adsorption/desorption, Eley–Rideal (ER) mechanisms, Langmuir–Hinshelwood (LH) mechanisms, etc. The representative models are Kurotaki's model,[10] Barbato's model,[11] Guerra's model,[12] etc.

Although great progress has been made in the modeling of the surface catalytic mechanisms, each model has its own empirical hypotheses, restrictions and uncertainty. Parameters in the model often come from the fitting of experimental results, lacking theoretical supports. In the light of this, Norman et al. [13,14] started from molecular dynamics (MD), and analyzed the reaction mechanisms between O and SiO_2 surface. In Norman's model, the model parameters depend on not only the experimental results, but also the results of MD simulations. It is found that only the defect site on the SiO_2 surface ($\equiv Si^\cdot$, $\equiv Si - O^\cdot$ and $\equiv Si–O_2$) can react with the impinging gas particles. Therefore, Norman et al.[13] at first considered only the reactions between O atom or O_2 and those three defect sites, and constructed the high temperature (HT) catalytic model. However, it is found that with the HT catalytic model, the catalytic efficiency is too much underpredicted in the low temperature range, as shown in Fig. 1(a). Thus, a low temperature (LT) model is built,[14] which considers the reactions in the physisorption zones and partial reactions

in the chemisorption zones. However, the problems still remain that with the HT model, the catalytic efficiency above 1000 K is quite lower than the experimental results, and cannot maintain continuity in the whole temperature range, as shown in Fig. 1(b). In Fig. 1, high (low) T model stands for the high (low) temperature catalytic model, RCG means reaction cured glass and FRC stands for finite rate catalytic model. Further analysis shows that those underpredictions may be due to not enough reaction mechanisms. Therefore, Norman's HT and LT models are combined to construct a new surface catalysis model in this paper. The surface catalysis mechanism will be also analyzed with this model.

2. Physiochemical model

2.1. Physiochemical reactions

The surface catalysis model constructed in this paper is based on Norman's HT and LT models; therefore, it belongs to the third type of catalysis models, namely the CSC model. As shown in Table 1, it consists of eight reactions, with the first six reactions being reversible and the last two considering only the forward reactions. In Table 1, $[E_S]$ ($[E_F]$) is the concentration of the vacant chemisorption (physisorption) sites; $[O_S]$ ($[O_F]$) is the concentration of the atomic oxygen chemisorption (physisorption) sites; $[O_{2S}]$ is the concentration of O_2 chemisorption sites. The last three reactions in which the physisorption areas participate come from Norman's LT model, while the rest are from the HT model. Schematic diagrams of chemisorption reactions 1–5 are shown in Fig. 2(a)–(e), while the schematic diagrams of LH mechanisms is shown in Fig. 2(f), which will be analyzed detailedly in Section 2.3.

2.2. Reaction rates I: reactions involving impinging oxygen

For most of the forward reactions involving impinging oxygen, the pre-exponent coefficients and activation energy come mainly from the MD simulation results. With respect to O atom chemisorption, it is assumed that impinging oxygen
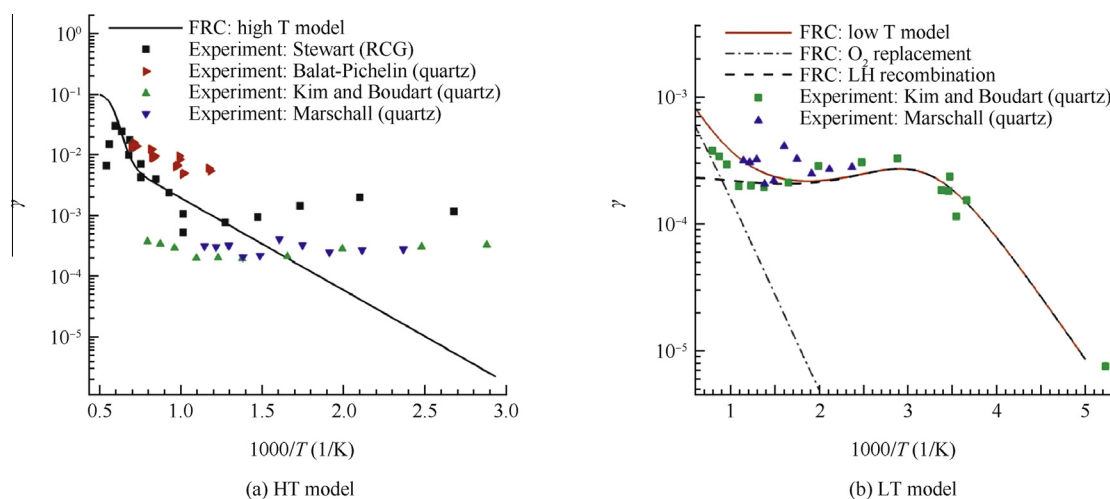

(a) HT model

(b) LT model

Fig. 1   Norman's surface catalysis model in comparison with the experimental results.