Oxygen Catalytic Recombination on Copper Oxide in Tertiary Gas Mixtures

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This paper presents experimental and theoretical results on catalytic phenomenon occurring in a test gas consisting of a mixture of 21% oxygen and 79% argon. The heat-transfer rates at the stagnation point of a blunt body are measured in a shock tube using a thin-film gauge. The surface of the test model was coated with silicon dioxide, copper oxide, or copper. The copper-coated model showed a heat-transfer-rate value 45% higher than that to a silicon-dioxide-coated model and 28% higher than that to a copper-oxide-coated model. The model surface was examined under a scanning electron microscope before and after the tests to confirm that the surface structure remained intact. The heat-transfer-rate formula obtained from the present analysis extends the theory of Goulard for a binary-gas mixture to a tertiary mixture. When the surface has low catalytic efficiency the tertiary formula gives nearly the same heat-transfer rate as Goulard’s formula, but when catalytic efficiency is high some differences are seen. Using this theoretical result, the experimental data are analysed. Catalytic efficiency of copper oxide is deduced to be 0.0026 to 0.0032, whereas copper has an efficiency of 0.016.

Nomenclature

\( c_p \) = specific heat at constant pressure, J/(kg-K)
\( \bar{c}_p \) = frozen specific heat at constant pressure, J/(kg-K)
\( c_v \) = specific heat at constant volume, J/(kg-K)
\( d \) = model diameter, m
\( D_{ij} \) = binary diffusion coefficient, m²/s
\( f \) = stream function
\( f' \) = velocity ratio
\( h \) = enthalpy, J/kg
\( h_i \) = frozen enthalpy, J/kg
\( h_R \) = heat of recombination, J/kg
\( I_c \) = constant electric current, A
\( J_i \) = rate of mass diffusion of species \( i \), kg/(m²-s)
\( k \) = Boltzmann constant, J/K
\( k_w \) = catalytic velocity, m/s
\( l \) = Chapman-Rubens constant
\( M \) = average molecular weight, kg/mol
\( m \) = average mixture mass, kg
\( M_i \) = molecular weight of species \( i \), kg/mol
\( m_{i_0} \) = particle mass of species \( i \), kg
\( M_{\infty} \) = freestream Mach number
\( n \) = number density, 1/m³
\( p \) = pressure, Pa
\( Pr \) = frozen Prandtl number, \( \mu c_p/\lambda \)
\( q \) = heat-transfer rate, W/m²
\( R \) = resistance, Ω
\( r_o \) = radial distance from axis of symmetry, m
\( s \) = reduced streamwise distance parameter
\( S_c \) = Schmidt number, \( \mu/\rho D \)
\( S_{c_{ij}} \) = binary Schmidt number
\( T \) = temperature, K
\( t \) = time, s
\( u \) = velocity along the wall, m/s
\( V \) = voltage, V
\( V_i \) = diffusion velocity of species \( i \), m/s

\( x \) = distance along the wall measured from the stagnation point, m
\( x_o \) = normal distance measured from the surface, m
\( X_i \) = molar fraction of species \( i \)
\( y \) = distance perpendicular to the wall measured from the wall, m
\( z \) = ratio of mass fraction, \( \alpha/\alpha_e \)
\( \alpha \) = mass fraction
\( \beta \) = stream velocity gradient, \( 1/s, da_e/dx \)
\( \beta_R \) = coefficient of resistivity, 1/K
\( \gamma \) = ratio of specific heats, \( c_p/c_v \)
\( \gamma_w \) = surface catalytic efficiency
\( \eta \) = boundary-layer coordinate normal to the wall
\( \lambda \) = thermal conductivity, W/(m-K)
\( \mu \) = viscosity, kg/(m-s)
\( \rho \) = density, kg/m³
\( \tau_{est} \) = nondimensional-flow-establishment parameter
\( \phi_1 \) = correction factor for catalytic effects of binary gas mixture
\( \phi_2 \) = correction factor for catalytic effects of tertiary gas mixture
\( \chi_{\Omega_{i,j}} \) = constant variable for \( \phi_2 \)

Superscript

\( ` \) = \( \partial/\partial \eta \)

Subscripts

\( C \) = conduction
\( D \) = diffusion
\( e \) = outer edge of boundary layer
\( \text{est} \) = flow establishment
\( i \) = \( i \)th component of mixture
\( j \) = \( j \)th component of mixture
\( s \) = stagnation point
\( st \) = steady flow
\( t \) = total
\( w \) = wall
\( \infty \) = freestream

I. Introduction

It is well known that surface catalytic phenomenon raises heat-transfer rates to solid surfaces. Goulard [1] laid a foundation for tackling this problem. A concise overview of catalysis-determination...
methods is given in a number of previous studies [2–6]. A considerable amount of experimental data exists on the catalytic phenomenon for oxygen and nitrogen on practical heat-shield materials [7–15]. These experiments are performed in arcjet wind tunnels. The results obtained in such arcjet wind-tunnel tests have been used in designing various heat-shield materials [8,10,12,15].

Surface catalytic phenomenon is used also in characterization of arcjet wind tunnels [7,9]. In an arcjet wind tunnel the average enthalpy can be determined by dividing the power input to the gas by the mass flow rate. But enthalpy is higher than the average enthalphy along the centerline of the nozzle flow and lower towards the nozzle wall. Therefore, in general, the enthalpy along the centerline where the tests are performed is unknown. This centerline enthalpy is determined usually using a copper calorimeter [7,9,10]. Copper is known as a highly catalytic material, and the catalytic efficiency of the copper surface is usually assumed to be about 0.17 [1]. The flow enthalpy is deduced using Goulard’s formula.

Difficulty arises because the surface of copper calorimeters become oxidized by the oxygen atoms with which it collides. Winkler et al. [16] found that the catalytic efficiency of a copper surface deteriorates very quickly once it is exposed to a dissociated oxygen stream. In the work of Park et al. [9] enthalpy of an arcjet wind tunnel is determined spectroscopically, and the resulting enthalpy value is fed into Goulard’s formula to deduce the catalytic efficiency of a copper calorimeter. Catalytic efficiency was determined to be about 0.01 by this method, which is a factor of 17 lower than that given by Goulard for copper and is believed to be that of copper oxide. There is also uncertainty about how rough the copper-oxide surface so formed is; the rougher the surface, the larger the effective catalytic efficiency [17]. A prolonged exposure of a copper surface may not only oxidize the surface but also roughen the surface. In order to determine the catalytic efficiency of such a rough surface [5], one needs first to know the value for a smooth surface. Therefore, the catalytic efficiency of the smooth copper-oxide surface is an important parameter in hypersonic technology.

The surface catalytic efficiency of copper oxide, however, has never been measured in a well-defined environment, i.e., in an environment where the enthalpy of the flow is known independently, the material is unmistakably copper oxide, and the surface is smooth. The surface needs to be exposed to an oxygen flow for only a short time in order to prevent roughening. Such a well-defined experiment can best be made in a shock tube. In a shock tube enthalpy of the flow is known from the shock speed. Measuring the heat-transfer rate in a shock tube is not new: experimental verification of the well-known Fay-Riddell formula [18] was made using a shock tube [19].

These are the reasons why the present research work is undertaken. In the present work, the heat-transfer rate to a blunt body with a copper-oxide surface is measured in a shock tube. In addition to the copper-oxide model, models with a silicon-dioxide surface and a copper-oxide model, models with a silicon-dioxide surface and a model with a copper surface have also been tested for comparison. Silicon dioxide is known as a noncatalytic material. The test gas was a 21% oxygen and 79% argon mixture, i.e., nitrogen in the air was substituted with argon. By doing so, the uncertainty associated with the possible surface reaction of atomic nitrogen was avoided.

Because Goulard’s heat-transfer-rate expression is applicable only to a monatomic oxygen/diatomic oxygen (O-O₂) binary mixture, a theoretical analysis had to be made to derive a heat-transfer-rate expression applicable to the present monatomic oxygen/diatomic oxygen/argon (O-O₂-Ar) tertiary mixture. The formula derived in the present work is similar to that of Goulard in that it produces an S-shaped relationship between heat-transfer rates and catalytic efficiencies, but it contains additional variable parameters. For low-catalytic surfaces the tertiary formula is found to be nearly the same as the binary formula, but for highly catalytic cases some differences are seen.

Towards the end of this paper, the experimental data are analysed using the tertiary-mixture heat-transfer-rate formula. From the analysis the catalytic efficiency of copper oxide is deduced to be about 0.0026 to 0.0032, which is about a factor of 7 smaller than Goulard’s value [1] of 0.02 and about a factor of 3.5 smaller than Park et al.’s value [9] of 0.01. Possible reasons are discussed.

Fig. 1 Schematic of the shock-tube experimental setup and its x-t diagram.
II. Test Equipment

A. Shock Tube

Figure 1 shows a schematic of the shock-tube experimental setup and its distance-time ($x$-$t$) diagram.

A diaphragm initially separated the driver tube from the transition piece and the driven tube. Internal diameters of the driver and the driven tubes were 6.8 and 4.75 cm, respectively. Their lengths were about 80 and 360 cm. The length of the transition piece was about 25 cm. A polyethylene film was used for the diaphragm. Its thickness was 0.35 mm. The driver-tube gas used was pure cold helium, and it was fed into the driver tube through a flexible copper pipe. The gas was supplied from a 12-MPa-filled bottle. The diaphragm ruptured in a passive manner at a driver-fill pressure of about $1.65 \pm 0.06$ MPa (absolute). The test gas was fed into the driven tube through a copper pipe connected to the transition piece.

Upon the rupture of the diaphragm, a primary shock wave was created and moved through the test gas in the driven tube. Test-gas length is defined as the distance between the primary shock and the head of the driver gas. An interface between the driver gas and the test gas is called a contact surface. The measurement was made in the steady flow region behind the primary shock wave. Vibrational excitation initiated immediately behind the primary shock and reached equilibrium within a few centimeters. Because the test-gas length was typically about 60 cm long in the shock tube used at a temperature of about 2050 K to 2850 K, it was assumed that thermochemical equilibrium was reached in this region. Shock speeds and wall static pressures were monitored using two PCB Piezotronics pressure transducers, denoted as $p_{t1}$ and $p_{t2}$, that were mounted in the wall of the driven tube.

When the primary shock reaches the experimental model an unsteady flow develops over the body, and a complex interaction of the primary shock wave and the shock wave produced by the model occurs. In front of the model, a steady bow shock wave eventually forms, and this shock wave is called a standing shock. Also, the flowfield behind the shock wave reaches a steady state. For this work, heat-transfer-rate measurements were made while the model was inside this steady flow. Duration of steady flow periods ranged from approximately $50 \mu s$ to $100 \mu s$ depending on flow conditions, after which the measurements became unreliable due to the arrival of the contact surface. The density behind the bow shock was much higher than the initial charging density because the standing shock flow had gone through the two normal shock waves. Therefore, it is relatively easy to obtain an equilibrium flow behind the standing shock.

B. Models

Two types of flat disk-cylinder models were used in the testing. One was for measuring surface heat-transfer rate at the stagnation point. The other was for stagnation-pressure measurement. The models were manufactured with stainless steel SUS 630. The heat-transfer models had an outer diameter of 12 mm and a length of 15 mm. The edge of the flat disk front face was rounded with a radius of 1.5 mm. The model was supported using a rear-mounted sting. An outer diameter of the sting was 9 mm, and its length was 400 mm. One heat-transfer gauge was flush-mounted at one time at the model center. Further details of the sensor are given in Sec. III.A.

The pressure model had an outer diameter of 20 mm and a length of 40 mm. The edge of the flat-disk front face was rounded with a radius of 3.0 mm. The model was supported by a rear-mounted sting. An outer diameter of the sting was 14 mm and its length was 383 mm. One 111A21 PCB piezoelectric pressure transducer was flush-mounted at the model center. Its sensitivity was $7.621 \text{ mV/kPa}$. Because the PCB transducer required a larger size than the size provided by the heat transfer model to be mounted, the slight difference in geometry and size of the pressure model was necessary.

Figure 2 shows the schematic of the experimental models.

As shown in the picture at the top the model can be seen through a sapphire window that was mounted in the driven tube section. During the test the front flat face of the model was located at about 5.0 mm upstream of the rear end of the sapphire window.
C. Test Conditions

For all tests the test gas in the driven tube was a mixture of 21% O₂ and 79% Ar by volume. Figure 3 shows a typical time history of the measured stagnation pressure. The steep initial rise of the signal is due to the arrival of the primary shock wave. The starting shock system corresponds to the complex interaction of the primary shock and the shock wave produced by the model. The flow then requires some time to establish, and within this time steady bow shock wave forms. After this period the flow becomes steady. In this work freestream flow properties were obtained by taking average values within this region. The steady-flow period ends due to the boundary-layer growth along the shock-tube wall. The duration of this region varies depending on conditions. Soon after the steady flow is disturbed by the boundary-layer growth, the contact surface arrives and terminates the flow.

Flow properties of the tested conditions were calculated using a Lagrangian one-dimensional code known as LID [20]. It is capable of calculating transient flow conditions in facilities such as shock tubes, light gas launchers, free-piston driven shock tunnels, or expansion tubes [20–23]. The code assumes that the flow is in thermal equilibrium. Thermodynamic and transport properties were calculated using a method suggested by Gordon and McBride used in the chemical equilibrium compositions and applications (CEA) program [24].

Table 1 summarizes the calculated steady flow conditions. The measured values of the wall static and stagnation pressures are also included for comparison. Tests were made at three different conditions named A, B, and C. The quantities p₁ and p₄ are the wall static pressures in the driven tube at positions indicated in Fig. 1. The shock speed uₛₜₒₜₜ was determined from the times these pressure sensors detected shock arrival. Assuming that the total enthalpy hₜ of the freestream is equal to the enthalpy at the boundary-layer edge, the boundary-layer-edge temperature Tₑₜ and the species mass fractions were calculated using an in-house thermochemical equilibrium code therm. This code is based on the method originally given by Gordon and McBride [24], but it uses the JANAF coefficients [25] with condition A the mass fraction of oxygen dissociated behind the bow shock was about 0.06. With condition B it was about 0.24. With condition C about two-thirds of the oxygen was dissociated. Close agreement was obtained between the measured wall pressures and the values calculated using the LID code.

### III. Heat-Transfer Gauge Details

#### A. Description of the Gauge

Surface heat-transfer rates at the stagnation point of the model were measured using low-resistance thin-film gauges. The gauges operate on the principle that resistance of a metal increases with temperature. Supplying a constant current across the metal, a change in resistance leads to the change in voltage according to the Ohm’s law. Such thin-film gauges have been used in many studies in aerothermodynamics of blunt as well as slender bodies at supersonic as well as hypersonic speeds [22, 23, 26–31].

Figure 4 shows a photograph and schematic of the thin-film gauge. It consisted of a thin-film of metallo-organic platinum type 5051, manufactured from ESL Electro Science, that was applied to the surface of a quartz substrate. The substrate had negligibly small thermal conductivity and low porosity. The diameter of the quartz used was 2 mm, and its length was about 8 mm. The platinum was hand painted on a front face of the quartz substrate using a single hair of a size 0 paint brush. A small strip of the platinum was then fired in a ThermoLyne 1400 furnace up to 850°C and stayed at the peak temperature for about 15 min. After this the substrate stayed in the furnace and cooled to room temperature overnight. The film width was about 0.4 mm. The approximate thickness of the fired-single-layer platinum film was about 150 to 250 nm. Toward both ends of the platinum film, metallo-organic gold type 8081-C, manufactured from ESL Electro Science, was hand painted and continued on the sides of the gauge. The gold was also fired in the furnace up to about 850°C. The approximate thickness of the fired-single-layer gold was less than 1000 nm. A heat-shrink tube was then used to insulate the gauge from the experimental model. The gauge was connected to electronic instrumentation such as a constant-current regulator, a differential amplifier, and a digital oscilloscope via a pair of standard enamel-coated copper wires. The outer diameter of the wires was about 0.1 mm. A small amount of soldering flux was applied to the tip of the wires to form rounded junctions. The wire tips were placed on top of the gold toward the rear end of the quartz substrate. The wire tips were held in position using the secondary heat-shrink tube. An araldite was then used to further strengthen the junction. The front face of the gauge was flush-mounted and level with the model surface.

#### B. Determination of Heat-Transfer Rates

The measured voltage using the thin-film gauge was converted to the surface heat-transfer rate through the direct semi-infinite technique [26]. This technique is based on the assumption of one-dimensional heat transfer through conduction into a thin metallic film. The film is to be deposited on a semi-infinite substrate of another material that is usually made of ceramic.
from the constant-current regulator.

resistance of the gauge at room temperature. For this work measured voltage the temperature assumed to have constant physical properties such as

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50 from about

\( T_{xo} \) \( \frac{Ro}{133} \) \( \frac{R}{136} \) \( \frac{d}{136} \) \( \beta \)

is temperature at distance \( x_o \) from the metallic film.

The principle assumes that the metallic film has negligible heat capacity and it is infinitely thin so that the film does not affect the temperature history of the substrate surface. Also, the substrate is assumed to have constant physical properties such as \( \rho, c_p, \) and \( \lambda. \) To follow the one-dimensional theory as best as possible the present quartz substrate must be long enough so that the heat transfer into the substrate becomes similar to that to the semi-infinite solid. Kinnear and Lu \[27\] noted that the semi-infinite assumption is well satisfied if the substrate thickness is greater than about 3 mm. With this length they reported that the substrate base-temperature-to-surface-temperature ratio is less than 1% over the long testing time of about 1 s.

Under these assumptions a numerical expression for the surface heat-transfer rate based on the time history of temperature can be obtained using the one-dimensional heat-diffusion equation \[26\]

\[
q(t_i) = \frac{2(\rho c_p \lambda)^{1/2}}{\pi^{1/2}} \sum_{n=1}^{\text{infty}} \frac{T(t_i) - T(t_{i-1})}{(t_n - t_{i-1})^{1/2}} + (t_n - t_{i-1})^{1/2}
\]  

(1)

where \( (\rho c_p \lambda)^{1/2} \) is known as the thermal product of the substrate. The measured voltage \( V \) from the thin-film gauge can be transformed to the temperature \( T \) using the relation

\[
T(t_i) = \frac{V(t_i)}{V_{\text{supply}} \cdot \beta_R}
\]  

(2)

In Eq. \( 2, V_{\text{supply}} = I_c \cdot R_e \) denotes direct current supply voltage from the constant-current regulator. \( I_c \) is the constant-current applied across the platinum film that is fed from the regulator. \( R_e \) is an initial resistance of the gauge at room temperature. For this work \( I_c \) was set at 10 mA. \( R_e \) varied depending on the gauge. Typically, it varied from about 50Ω to 200Ω. The coefficient of resistivity \( \beta_R = \frac{1}{R_e}(dR/dT) \) needs to be determined from gauge calibration. The calibration contained two-parts: one is static calibration and the other is dynamic calibration. The static calibration was conducted using a convection oven. Gauges were placed inside the oven and temperature was raised up to 45°C within 3 h. Gauge-resistance values were recorded at an interval of 5°C. Using this method the gauges were individually calibrated. Typically, \( \beta_R \) varied from about 0.002/K to 0.0023/K. The thermal product \( (\rho c_p \lambda)^{1/2} \) was determined to be about 1510 ± 100 W/K/m²/K through the dynamic calibration using the shock tube. The obtained value is very similar to the existing quartz-substrate data of Shultz and Jones \[26\] and Hayne \[31\] Detailed information regarding the static- and dynamic-calibration procedures is given by Kinear and Lu \[27\].

IV. Catalytic and Noncatalytic Walls

In total five different surfaces were used for the heat transfer experiment. The first of these had no surface coating. The purpose of this model was to test whether surface coating changes temporal response of the gauges. By comparing the results of this model with that of a coated model it was confirmed that the surface coating was indeed sufficiently thin, and so the thin-film-gauge principle given in Sec. II A is applicable.

The second model was coated with silicon dioxide (SiO₂), which is regarded as a noncataletic material. The SiO₂ was coated using an electron-beam (E-Beam) evaporation technique through the process of physical vapor deposition under high vacuum. When evaporating the SiO₂ source the experimental model was kept at room temperature. The SiO₂ source had a purity of 99.99%, purchased from Thin Films and Fine Materials (THIFINE). A deposition rate was set at about 0.3 nm/s. It was coated to a thickness of 500 ± 50 nm.

The third model consisted of two surface-coated layers first coated with the SiO₂ and then with copper oxide (CuO). The SiO₂ was first coated to a thickness of 500 ± 50 nm. Again using the E-Beam technique the CuO was coated on top of the SiO₂ layer to a thickness of 180 ± 70 nm. The CuO source had a purity of 99.9%, purchased from Leeschem International Co., Ltd. The distance between the CuO source and the target model where the material was coated was about 65 cm. When depositing the CuO the copper (Cu) and monatomic oxygen (O) was not a perfect 1:1 ratio, but instead it was slightly Cu rich. To keep the 1:1 ratio as best as possible oxygen gas was constantly injected into the vacuum chamber at the flow rate of 10 sccm. The SiO₂ was used as the intermediate layer because this material is known to be electrically nonconductive. The SiO₂ layer protects from becoming short-circuited between the neighbouring layers.

The fourth model was coated with two layers: SiO₂ and Cu. The SiO₂ was first coated on the model surface to a thickness of
500 ± 50 nm. Then Cu was coated over the SiO$_2$ layer to a thickness of 180 ± 20 nm. The Cu source had a purity of 99.998%, purchased from THIFINE. Unlike the case of the CuO the evaporation of the Cu was conducted under high vacuum without injection of oxygen gas. Therefore, the coating process is clearer and simpler, so it is reasonable to regard the process to be inert from oxidation. With the SiO$_2$ thickness used, however, the thin-film gauge became short-circuited so that measurement could not be made. Because the problem could be due to the sensor that was used, seven different gauges have been tried, but the results were the same. Several explanations are possible. The first is that the Cu layer is physically touching the platinum film. The second is that the Cu layer is touching the gold at the edges of the gauge. The third is the combination of the two.

In order to solve this short-circuiting problem an attempt was first made by coating the SiO$_2$ on the fifth-model surface by doubling the layer thickness to 1000 ± 50 nm. For this attempt four different gauges were tried. The thickness of the Cu was kept the same. Unfortunately, all the gauges again became short-circuited and so measurement could not be made. The second attempt was made using the same thickness SiO$_2$ = 1000 ± 50 nm, Cu = 180 ± 20 nm, but with this case a tiny amount of 5-min araldite was placed on top of the gold at both ends of the thin-film-gauge surface before coating. Three different gauges were tried. One was successful. It was not short-circuited and so the heat-transfer measurement was made successfully. With this successful one, there was a negligible amount of change in resistance across the platinum film. After one shot, however, the platinum film again became short-circuited. No further measurement was attempted.

Figure 6 shows the heat-transfer models with and without surface coatings. The first model in the top row of the figure shows the model without surface coating. As seen the heat-transfer gauge was flush-mounted at the model center. The second model in the same row shows the SiO$_2$-coated surface. The surface shows a transparent green color. The CuO-coated surface shows a reddish-brown color which is the third model in the same row. The two models in the bottom row show the models with Cu-coated surface. The coatings show a brown color. Because the background-light intensity used was slightly different between the two photos, the contrast of their surface colors looks a little different. The right-hand side Cu-coated model shows tiny blobs of the 5-min araldite placed on top of the gold at both ends of the thin-film-gauge surface. The height of the araldite blobs used was measured to be less than 0.3 mm. For all five models a cylindrical side was wrapped using an insulating tape before coating so that there is no change in color on this side after evaporation.

A. Without Coating

Before depositing the platinum film and coating various materials on the model surface, it was important to make sure that the quartz substrate is smooth and highly polished. The polishing process is essential because geometric sharp irregularities and discontinuities at the surface, such as fine cracks and/or cavities, can possibly produce faulty sensors [27].

The substrate was first polished using 600-grit abrasive silicon-carbide (SiC) sandpaper mounted on a rotating flat-disk. The disk was set to rotate at 350 rpm. The smoothing was then continued using 1200- and 2000-grit sandpapers. Care was taken to ensure that the surface remained flat and level. For all the cases the grits were required to have a constant stream of 1-μm-particle-size filtered water as lubricant to wash away swarf. The polishing process was completed using a crocus cloth mounted on the rotating disk. A 6-μm diamond suspension was used as the lubricant. Approximately, it took 2 h for the polishing: 20 min with 600 grit, 20 min with 1200 grit, 20 min with 2000 grit, and about 1 h with the crocus cloth. After the polishing the substrate was washed with ethanol and filtered water. It was then placed under a heating lamp to dry.

Figure 7 shows micrographs of the surface of the quartz substrate before and after the polishing. They were taken at x80 magnification using a Lagerfeld metallographic microscope ME 79013. A Nikon COOLPIX 5000 camera was used to obtain the images. The x1000 and x10,000 images were taken using a Magellan 400 scanning electron microscope (SEM). Because the quartz is an electrically nonconductive material, Platinum P-100 manufactured by ELCOAT was used as the coating material to make the surface electrically conductive. Platinum was sputtered on the surface to a thickness of about 5 nm.

The micrographs and the SEM images before the polishing show that the substrate has numerous scratches, marks, and dents. Looking at the x1000 images both before and after the polishing the dark gray regions are stains that arose from the surrounding environment. Surface quality seems greatly improved by polishing. In the x10,000 image there are still a number of noticeable scratches on the surface. However, considering that the size of the horizontal axis of this image is 12.8 μm, these scratches are in a scale of a micrometer or less.
Because the present gauges were all successful in producing the right range of electrical resistances across the platinum film, this quality of surface finish seems reasonable for the present heat-transfer measurement.

Figure 8 shows micrographs and SEM images of the surface of the platinum heat-transfer gauge before and after about five shots of condition A experiment. It is to be noted that, before the experiment, the model was sealed using a small plastic bag so as not to expose it to the surrounding environment. It was opened just before the experiment. Figure 9 shows an x-ray spectrum of the surface of the platinum heat-transfer gauge before and after the experiment. Elemental compositions were analysed using an APOLLO XPP Energy-dispersive x-ray spectrometer that was attached to the SEM.

In the Figs. 1 and 2 denote locally scanned areas indicated in Fig. 8. Before the test region I was composed mainly of platinum Pt. After the test, there seems to be a noticeable increase in the level of carbon C and atomic oxygen O. There is also a slight increase in the level of silicon Si. Considering the C was not used for the driver nor the driven tube gas, it was thought that the C flew from the shock-tube wall and stuck onto the model surface after a few shots of experiment. An increase in the level of Si and O indicates that the Pt surface was stripped during the test, and that the quartz substrate is exposed in this stripped region.
Fig. 11  X-ray spectrum of the silicon-dioxide-coated surface. Before experiment (solid line); After experiment (dashed line).

Fig. 12  Micrographs and SEM images of the copper-oxide-coated surface.

Fig. 13  X-ray spectrum of the copper-oxide-coated surface. Before experiment (solid line); After experiment (dashed line).

Fig. 14  Micrographs and SEM images of the copper-coated surface.
B. With Coatings

Micrographs, SEM images, and x-ray spectra similar to those shown in the preceding section have been taken also for the SiO$_2$-coated, CuO-coated, and Cu-coated models. Figures 10 and 11 show the SiO$_2$ results. Figures 12 and 13 show the CuO results. Figures 14 and 15 show the Cu results. As seen in the results for all three models there was a negligible amount of O from the incoming flows that sticks on the surface during the test.

O$_2$ can be formed through two different modes. One is known as a homogeneous mode. This mode occurs when two incoming O atoms collide and form O$_2$ with the help of the surface atoms acting as a third body. The second mode is a heterogeneous mode. In this mode solid molecules at certain sites on the surface donate one atom to an incoming colliding atom, e.g., SiO$_2$ + O $\rightarrow$ SiO$+$ O$_2$. The fact that not much change occurs in surface oxygen concentration suggests that homogeneous recombination is dominant.

A feature to note from the x10,000 magnification SEM images of the SiO$_2$ and the Cu surfaces is that their particles seem to be deposited quite regularly and uniformly. The CuO-coated surface, however, shows noticeable differences in the size of the deposited particles when compared with their neighbors. The particles seem to form an amorphous structure, so they lack the long-range characteristic of a crystalline solid.

V. Measured Heat-Transfer Rates

A. Condition A

Figure 16 compares the measured surface heat-transfer rates of the uncoated, SiO$_2$-coated, and CuO-coated models for condition A (at $h_t = 1.92$ MJ/kg). The measured stagnation pressure is also included to indicate the steady-flow period. For both the pressure and the heat-transfer rate signal traces based on multiple shots are presented to show shot-to-shot repeatability. In the two figures in the top row, est denotes flow establishment and st denotes steady flow. In the three figures in the bottom row, the averaged value of heat-transfer rate within steady flow is indicated at the bottom right of each figure. The uncertainty ($\pm$) denotes a shot-to-shot variation of the steady heat-transfer rate based on the 95% confidence interval.

The steep gradients of the signals in the beginning of the flow are due to the primary shock arrival for both pressure and heat-transfer rate. Looking at the primary-shock-arrival region the response/delay times of the thin-film gauges, uncoated or coated with different materials, do not show much difference. For both the pressure as well as the heat-transfer rate the flows became steady at approximately 180 $\mu$s with respect to the shock arrival. This can be expressed in terms of a nondimensional flow-establishment parameter

$$\tau_{est} = \frac{t_{est} \cdot u_\infty}{d}$$ (3)

where $t_{est}$ denotes the time to reach steady flow measured from the primary shock arrival, $u_\infty$ is the freestream velocity, $d$ is the model diameter, and $\tau_{est}$ indicates the number of body diameters required to reach a steady state. Using this relation it is found that the pressure and the heat-transfer models required about 12 and 19 body diameters to reach a steady state.

In the heat-transfer data there are not many variations in the level of the steady-heat-transfer rate for all the cases. The CuO-coated model...
value is about 5% and 3% higher than the uncoated and the SiO2-coated models, respectively. This is well within the realm of the experimental uncertainty. This small difference is understandable because the postshock temperature induced for this condition is not high enough to cause a noticeable level of chemical reaction, and as a consequence, the heat transfer to the wall solely depends on molecular conduction.

B. Condition B

Figure 17 compares the measured surface heat-transfer rate of the SiO2-coated and the CuO-coated models and the stagnation pressure for condition B (at \( h = 2.66 \) MJ/kg). The flow became steady at approximately 140 \( \mu \)sec with respect to the shock arrival for this case. This is equivalent to about 11 and 18 body diameters of the flow for the pressure and the heat-transfer models, respectively.

In contrast to the condition A data some differences are found in the level of the steady heat-transfer rate between the SiO2-coated and the CuO-coated models. The CuO data shows about 9% higher in heat transfer than the SiO2 data. With condition B, the mass fraction of oxygen dissociated behind the bow shock wave is about 0.24. Negligible amount of oxidation occurs on the surface, i.e., \( O + SiO_2 \rightarrow O_2 + SiO, \) \( O + CuO \rightarrow O_2 + Cu, \) and \( O + O + Cu \rightarrow O + CuO, \) and this rise in the measured heat-transfer rate can be thought to be the consequence of catalytic recombination of two incoming O-atoms.

C. Condition C

Figure 18 compares the measured surface heat transfer rate of the SiO2-coated, the CuO-coated, and the Cu-coated models for condition C (at \( h = 4.24 \) MJ/kg).

As the figures show the flow became steady at about 130 \( \mu \)sec after shock arrival. This is equivalent to about 13 and 21 body diameters of the flow. In accordance with the condition-B data, some differences in the level of the steady heat-transfer value are found between the SiO2-coated, the CuO-coated, and the Cu-coated cases. The CuO data shows about 13% higher in heat transfer than the SiO2 data. On the other hand, the Cu data shows a considerably higher heat-transfer rate. It is about 45% and 28% higher than the SiO2-coated and CuO-coated cases, respectively.

VI. Stagnation-Point Heat-Transfer Rate to a Catalytic Surface

A. Theoretical Analysis

Because Goulard’s work is well known, it will not be discussed here. It suffices, for the purpose of later reference, only to mention a few points. Goulard’s work is for the heat-transfer phenomenon occurring in the stagnation region of an axially symmetric blunt body flying at a hypersonic speed. Newtonian hypersonic approximation is used in determining the pressure distribution. The flow is in thermochemical equilibrium at the edge of the boundary layer. Inside the boundary layer the flow is chemically frozen. Across the boundary layer the product of density and viscosity remains constant, i.e., \( \frac{\rho \mu}{\rho_e \mu_e} = 1. \) Prandtl number and Schmidt number remain constant also. The distance from the wall is describable using a dimensionless coordinate \( \eta \) and the velocity field is describable using a dimensionless function \( f. \) The \( \eta \) and \( f \) are expressed as

\[
\eta = \frac{u_e}{\sqrt{2s}} \int_0^\gamma r_e \rho dy
\]

(4)

\[
f' = \frac{\partial f}{\partial \eta} = \frac{u}{u_e}
\]

(5)

where \( s \) is a reduced streamwise distance parameter

\[
s = \int_0^x \mu_e u_e r^2 dx
\]

(6)

Because the intention of the present work is to extend Goulard’s theory to a tertiary mixture, all these assumptions are kept in the present work. By doing so the results of the present work will serve as an incremental improvement to Goulard’s theory.

---

Fig. 17 Measured surface heat-transfer rates and stagnation pressure for condition B.
According to Goulard’s analysis [1], the stagnation-point heat-transfer rate becomes

\[ q = q_C + q_D \]  

(7)

where \( q \) is the total heat transfer to the wall, \( q_C \) is heat transfer by conduction, and \( q_D \) is heat transfer by diffusion. The \( q_C \) and \( q_D \) are written as

\[ q_C = 0.47\sqrt{2\mu_\infty\rho_\infty^2\overline{h}_{sc}} \]  

(8)

\[ q_D = 0.47\overline{Sc}^{-2/3}\sqrt{2\nu_\infty\rho_\infty\overline{h}_{sc}\varphi_1} \]  

(9)

where \( \varphi_1 \) is a correction factor for catalytic walls

\[ \varphi_1 = \frac{1}{1 + (0.47\overline{Sc})^{-2/3}\sqrt{2\mu_\infty\rho_\infty\nu/\nu_\infty}} \]  

(10)

\( \varphi_1 = 0 \) corresponds to a non-catalytic wall and \( \varphi_1 = 1 \) corresponds to a fully catalytic wall.

In the tertiary mixture under consideration the diffusion mass flux and velocity involve six binary diffusion coefficients \( D_{ij} \). According to the Chapman-Enskog theory the diffusion velocity \( V_i \) becomes [32]

\[ V_i = \frac{n}{\rho X_i} \sum_j \left( m_j D_{ij} \frac{\partial X_j}{\partial y} \right) \]  

(11)

where \( D_{ij} \) is expressed as [32]

\[ D_{ij} = \frac{kT}{p_l(8/3)\sqrt{2m_i m_j/\pi kT(m_i + m_j)}}\overline{\Omega}_{ij}^{(1,1)} \]  

(12)

Here \( \overline{\Omega}_{ij}^{(1,1)} \) is the diffusion-collision integral for an interaction pair of \( i \)th and \( j \)th components of the mixture. For this work the required integral values were obtained from Kim et al. [33].

Using the relations \( z_j = \alpha_j/\alpha_{ei}, \alpha_j = X_j(M_j/M) \), and Eq. (4), Eq. (11) can be rearranged as

\[ V_i = \frac{\rho u_s r_0}{\sqrt{2sX_i}} \sum_j \left( \frac{m_j M_j}{m_i M_i} D_{ij} \varphi_{1i} \right) \]  

(13)

Then the gradient of mass flux of species \( i \) becomes

\[ \frac{\partial}{\partial y} (\rho_i V_i) = \left( \frac{\rho u_s r_0}{\sqrt{2s}} \right)^2 \sum_j \left( \frac{\alpha_{ij} m_j M_j}{X_i m_i M_i} \rho_i D_{ij} \varphi_{1i} \right) \]  

(14)

Introducing binary Schmidt number \( \overline{Sc}_{ij} \) for an interaction pair of the \( i \)th and \( j \)th component of mixture

\[ \overline{Sc}_{ij} = \frac{\mu}{\rho D_{ij}} \]  

(15)

and using Eq. (6), the mass relation \( (M_i/M_j = m_i/m_j) \), and the Chapman-Rubesin constant \( l \)

\[ l = \frac{\rho \mu}{\rho_i \nu_\infty} \]  

(16)

the gradient of mass flux of species \( i \) shown in Eq. (14) can be expressed as

\[ \frac{\partial}{\partial y} (\rho_i V_i) = \frac{\rho \alpha_{ei} u_s}{2s} \sum_j \left( \frac{\alpha_{ij} m_i l}{\alpha_{ei} m_i \overline{Sc}_{ij} \varphi_{1i}} \right) \]  

(17)

Then, for the tertiary gas mixture \( (i = 1, 2, 3 \) and \( j = 1, 2, 3) \), the conservation equation of species mass written in Goulard [1] can now be expressed as

\[ f z_i = (A_{11} z_i + A_{12} z_j + A_{13} z_k)' = 0 \]  

(18)

\[ f z_i = (A_{21} z_i + A_{22} z_j + A_{23} z_k)' = 0 \]  

(19)

\[ f z_i = (A_{31} z_i + A_{32} z_j + A_{33} z_k)' = 0 \]  

(20)

where
A_{11} = \left( \frac{\alpha_2 m_1}{\alpha_1 m Sc_{11}} \right) A_{12} = \left( \frac{\alpha_2 m_1}{\alpha_1 m Sc_{12}} \right) A_{13} = \left( \frac{\alpha_2 m_1}{\alpha_1 m Sc_{13}} \right) A_{21} = \left( \frac{\alpha_2 m_2}{\alpha_1 m Sc_{21}} \right) A_{22} = \left( \frac{\alpha_2 m_2}{\alpha_1 m Sc_{22}} \right) A_{23} = \left( \frac{\alpha_2 m_2}{\alpha_1 m Sc_{23}} \right) A_{31} = \left( \frac{\alpha_2 m_3}{\alpha_1 m Sc_{31}} \right) A_{32} = \left( \frac{\alpha_2 m_3}{\alpha_1 m Sc_{32}} \right) A_{33} = \left( \frac{\alpha_2 m_3}{\alpha_1 m Sc_{33}} \right)

\text{For the case where the third gas species is chemically inert (}z_1^0 = 0\text{) and the coefficient of self-diffusion }D_{ii}\text{ is zero, Eqs. } (18-20) \text{ become}

\begin{align*}
f z_1' - A_{11} f z_1'' & = 0 \\
f z_2' - A_{12} f z_1'' & = 0 \\
-A_{31} z_1'' - A_{32} z_2'' & = 0
\end{align*}

\text{Rearranging Eq. } (23)

\begin{align*}
z_1'' & = \frac{A_{32}}{A_{31}} z_2'' \\
z_2'' & = \frac{A_{31}}{A_{32}} z_1''
\end{align*}

\text{Substituting Eq. } (25) \text{ into Eq. } (21) \text{ yields}

\begin{align*}
f z_1' - A_{12} \left( - \frac{A_{31}}{A_{32}} z_2'' \right) & = 0
\end{align*}

so that

\begin{align*}
z_1'' + \phi_1 fz_1' & = 0
\end{align*}

where \(\phi_1 = A_{12}/(A_{12}A_{32})\) is the constant based on the boundary-layer-edge conditions.

Concerning species \(i = 2\) a similar expression can be obtained by substituting

\begin{align*}
f z_2' - A_{21} \left( - \frac{A_{32}}{A_{31}} z_1'' \right) & = 0
\end{align*}

so that

\begin{align*}
z_2'' + \phi_2 fz_2' & = 0
\end{align*}

where \(\phi_2 = A_{12}/(A_{12}A_{32})\) is also the constant based on the boundary-layer-edge conditions.

In Eqs. \(27\) and \(29\) the required \(f\) values were obtained from similar solutions of momentum equation \([1]\)

\begin{align*}
f f'' + ff'' & = 0
\end{align*}

with the boundary conditions of \(f(0) = f'(0) = 0\) and \(f'(\infty) = 1\).

Eq. \(30\) was solved using a shooting method \([34]\). The equation was iterated by assuming initial values for \(f''(0)\). After iterating using several sets of the initial values, a Newton-Raphson interpolation scheme was used to estimate the next guess of the initial values. The process was repeated until the following boundary conditions were satisfied. The equation was solved for the interval \(0 \leq \eta \leq 6\) with 100 node points across \(\eta\). The iterations were terminated when \([1 - f'(\infty)] \leq 10^{-6}\). The convergence of the solution was checked by doubling the size of \(\eta\), and it was found that the difference was negligible.

Recalling Eq. \(11\), after some rearranging, the mass flux of species \(i\) at the wall can be written as

\begin{align*}
\left(J_i\right)_w = (\rho_i V_i)_w = \frac{\rho_i \alpha_i}{\sqrt{\left(\mu_i \rho_i/2\beta\right)}} \sum_j \left( \frac{\alpha_j m_j}{\alpha_i m} \rho_j D_{ij} z_j' (0) \right)
\end{align*}

where \(\frac{\beta}{\rho_i \mu_i} \approx \frac{\beta}{\rho_i \mu_i} \text{ after Goulard } [1]\).

Imposing \(z_j' (0) = 0\) and the coefficient of self-diffusion \(D_{ii}\) is zero, Eq. \(31\) becomes

\begin{align*}
\left(J_i\right)_w = (\rho_i V_i)_w = \frac{\rho_i \alpha_i}{\sqrt{\left(\mu_i \rho_i/2\beta\right)}} \frac{\alpha_i m_i}{\alpha_i m} \rho_i D_{ii} z_i' (0)
\end{align*}

The species mass flux \((J_i)_w\) can also be expressed in terms of catalytic velocity \(k_{w1}\) for species \(i = 1\),

\begin{align*}
\left(J_i\right)_w = (\rho_i V_i)_w = -\rho_i \alpha_i k_{w1} = -\rho_i \alpha_i k_{w1} z_i (0)
\end{align*}

\begin{align*}
\left(J_i\right)_w = (\rho_i V_i)_w = \rho_i \alpha_i k_{w1} = \rho_i \alpha_i k_{w1} z_i (0)
\end{align*}

Here the mass flux of the species \(i = 1\) has the equal magnitude to that of the species \(i = 2\), but they are opposite in direction because the third species is chemically inert.

According to the kinetic theory the \(k_{w1}\) is defined as

\begin{align*}
k_{w1} = \frac{\gamma_w}{4} \sqrt{\frac{8kT_w}{\pi m_1}}
\end{align*}

where \(\gamma_w\) is the surface catalytic efficiency defined as the ratio of the number of atoms recombining on a surface per unit area and time to the total number of atoms striking the surface per unit area and time.

The chemical-energy-accommodation coefficient is defined as the ratio of the chemical energy transferred to the surface by recombination to the total energy due to the recombination of atoms. Because the near cold wall was considered in this work, and the energy level of the oxygen atoms is at the ground state, it was assumed that the energy-accommodation coefficient is unity and the oxygen atoms have complete accommodation of the released chemical energy.

Combining Eqs. \(33\) and \(35\) yields

\begin{align*}
z_1(0) = \frac{m}{m_2} \frac{\mu_j \rho_j}{2\beta} \frac{k_{w1}}{\rho_j D_{w1}} z_1(0)
\end{align*}

Integrating Eq. \(27\) in two steps gives

\begin{align*}
z_1(\eta) - z_1(0) = z_1(0) \int_0^\eta e^{-\phi_1} f z_1'' d\eta = z_1(0) \int_0^\eta \left( f''(\eta) \right) d\eta
\end{align*}

at \(\eta \to \infty\), \(z_1(\infty) = 1\). Using this boundary condition Eq. \(38\) becomes

\begin{align*}
z_1(0) = \frac{1}{\phi_1} [1 - z_1(0)]
\end{align*}

where
Manifested in Eq. (10), but there is an additional variable parameter \( \chi \). For the case of the binary gas \( \chi \) is equivalent to \( 0.475 S_{\gamma}^{-2/3} \).

### B. Comparison with Experiment

Figure 20 shows the dependence of heat-transfer rate on the surface catalytic efficiency for conditions B and C. Condition-A data exhibited low temperature behind the bow shock wave at which chemical reaction does not occur noticeably. Hence, the data is not presented here. In the figure \( q_C \) and \( q_D \) denote heat transfer due to conduction and diffusion, respectively. The \( q_C \) was calculated using the relation defined in Eq. (8). In the calculation, the boundary-layer-edge values were again obtained from using the thermo code. Because the code does not calculate viscosity, the viscosity was obtained using the CEA program [24] with \( \nu \) and \( T_e \) as inputs. For the given conditions there were very small differences in the calculated density and the species compositions between the two codes. The frozen Prandtl number at the wall \( Pr_w \) was obtained using the equilibrium value at the boundary-layer edge using the CEA program.

The \( q_D \) was calculated using Eqs. (9) and (44) for the binary and the tertiary gases, respectively. For the binary-gas calculation the Goulard’s assumption of \( S_C = 0.485 \) was used. For the tertiary gas the required diffusion-collision-integral values for the calculation of binary Schmidt number \( S_{Cij} \) were obtained from Kim et al. [33].

Determination of the effective nose radius of flat-faced models is required when calculating the stagnation velocity gradient \( \beta = dU/dx \). The data of Zoby and Sullivan [35] are based on air flows and at high Mach numbers. Because the present work is based on the \( \text{O}_2-\text{Ar} \) gas mixture and at low Mach numbers less than 2, the author believed that the use of the Zoby and Sullivan data in determining the velocity gradient is somewhat not warranted at least
for the present conditions. Therefore, in this work, the velocity gradient was determined using the Goulard’s conductive heat-transfer-rate equation defined in Eq. (8) by substituting the calculated boundary-layer-edge values and the measured surface heat-transfer rates for the SiO$_2$-coated wall into the equation. In this way the issues related to the effective nose radius can be avoided.

Because the present data is based on the O$_2$-Ar mixture as well as at low Mach numbers, there is no literature value of the velocity gradient that can be used for the theoretical noncatalytic heat-transfer-rate calculation. One might think that the stagnation velocity gradient can be determined using CFD. But, because of the singularity at the axis, CFD can not be trusted at the stagnation point to the accuracy intended here. Therefore, although the assumption that SiO$_2$ is noncatalytic is not totally correct, it was used for the present investigation.

The experimental data for the Cu-coated and the CuO-coated walls are also included for comparison. For the case of the Cu-coated wall $q_D$ in Fig. 20 is defined as the difference between $q_{\text{Cu}}$ and $q_{\text{SiO}_2}$. For the case of the CuO-coated wall $q_D$ is defined as the difference between $q_{\text{CuO}}$ and $q_{\text{SiO}_2}$. It is to be noted that the Cu-coated wall data is presented only for the case of condition C because there is no data for condition B.

Referring to the theoretical heat-transfer distributions for condition B in Fig. 20, the binary as well as the tertiary gases show that the heat-transfer ratio is zero when the wall is noncatalytic, say at a very low value of $\gamma_w \approx 10^{-5}$. At about $10^{-5} \leq \gamma_w \leq 10^{-3}$, both show a gradual increase and the difference between them is almost negligible. Beyond this region, heat transfer rises quite rapidly to about $\gamma_w \approx 10^{-1}$ for both. They then tend to plateau to their constant values toward the fully catalytic wall at $\gamma_w = 1$. In the region where $\gamma_w$ is greater than or equal to $10^{-2}$, some differences between the two are found. At $\gamma_w = 1$, the tertiary gas shows about a 7% higher heat-transfer rate than the binary gas. Concerning the condition C result the heat-transfer distribution shows a trend similar to that of condition B. Similar to the condition B result the condition C also shows that the binary and the tertiary gases start to deviate at about $\gamma_w = 10^{-2}$. The differences then become gradually larger until the wall becomes fully catalytic. At $\gamma_w = 1$ the tertiary gas again shows about a 3% higher heat-transfer rate than the binary gas. This level of difference is not a universal property of tertiary gases, but it is a function of relative concentrations and relative binary diffusion coefficients.

The experimental surface catalytic efficiencies were determined by finding intersection points between the measured and the calculated heat-transfer rates. Using this method the efficiency for the CuO-coated wall is determined to be about 0.0026 and 0.0032 for conditions B and C, respectively. In the case of the Cu-coated wall for condition C the efficiency is determined to be about 0.016 using the binary- and the tertiary-gas approaches.

Comparing the present efficiencies to the existing data of Goulard [11] it is seen that the present values for the Cu and the CuO walls are about a factor of 11 and 7 lower, respectively. Compared to the CuO data of Park et al. [9] the present value is about a factor of 3.5 lower. The prolonged exposure of a Cu surface in a dissociated oxygen flow may not only oxidize the surface but also roughen the surface. Then, considering that: 1) the inflow condition used in Park et al. [9] consisted of high enthalpy at 40.6 MJ/kg in air where nearly all oxygen were dissociated; and 2) the experiments were conducted in a long-flow duration arcjet facility, it seems clear that their oxidized Cu surface was rough. Contrarily, the present experiments were based on a smooth wall where the surface was highly polished up to a scale of a micron or less. Because the number of collisions of dissociated oxygen particles on a rough surface is expected to be higher than that to the smooth wall, it seems quite certain that the effective surface catalytic efficiency of the present case is lower. Further comparison and discussion about the catalytic efficiency between the present values to the existing data is made in Sec. VLC.

Figure 21 shows the dependence of heat-transfer rate on the surface catalytic efficiency for the O$_2$-N$_2$ interaction. It is assumed that the test gas contains a 21% oxygen and 79% nitrogen mixture by volume. For this hypothetical case the total enthalpy $h_t$ of the freestream and the stagnation pressure behind the bow shock $p_s$ that were used in the O$_2$-N$_2$ case are again adopted here, but the third gas species Ar is substituted by N$_2$. The validity for assuming N$_2$ as chemically inert [so that $\gamma_s(0) = 0$] for the tertiary-gas calculation seems reasonable because the temperatures induced behind the bow shock in the present instance were not high enough to cause N$_2$ dissociation. At such $h_t$ and $p_s$, there will be about 6% of nitric oxide NO by mass that would be present in the airflow stream for both conditions B and C. In the calculations, to estimate the amount of O atoms present in the gas as best as possible, the mass fraction of NO is book-kept as N$_2$. Therefore, applying the present heat-transfer relation in air could introduce some uncertainty in the interpretation of data.

With regard to both the binary and the tertiary cases the boundary-layer-edge values were calculated using the CEA program. Ionization effect in the flow stream was assumed to be negligible. The required diffusion-collision-integral values were again obtained from Kim et al.[33]. Because the purpose of showing the O$_2$-N$_2$ mixture results is to make a comparison between the binary- and tertiary-gas approaches, the stagnation velocity gradient $\beta$ used in the O$_2$-Ar interaction case was again used here.

Referring to Fig. 21 the binary and the tertiary gases show that the heat-transfer ratio is zero when the wall is noncatalytic, say at a very low value of $\gamma_w \approx 10^{-5}$. Up to about $\gamma_w \approx 10^{-2}$ the difference between the two is small. At about $10^{-4} < \gamma_w < 10^{-3}$ both cases show a gradual increase, and beyond this region heat transfer rises quite rapidly to about $\gamma_w \approx 10^{-1}$. They then tend to plateau to their constant values toward the fully catalytic wall at $\gamma_w = 1$. In the case of $T_e = 3500$ K and $p_s = 330$ kPa the binary and the tertiary gases show some differences beyond $\gamma_w$ of about $10^{-2}$. At $\gamma_w = 1$, the tertiary gas shows about an 18% higher heat-transfer rate than that to the binary gas. In the case of $T_e = 4000$ K and $p_s = 225$ kPa at $\gamma_w = 1$ the tertiary gas shows about a 16% higher heat-transfer rate than that of the binary gas. This level of difference is due to the difference in binary diffusion coefficients between the binary and the tertiary gases.

C. Surface Catalytic Efficiency

Figure 22 presents measured surface catalytic efficiency $\gamma_w$ of Cu and CuO from various sources including the present data. The open symbols denote experimental data for Cu walls. The filled symbols denote experimental data for CuO walls. Concerning the present data $T_w$ denotes the measured average thin-film-gauge temperature during steady flow. The vertical error bar denotes a shot-to-shot variation of the measured temperature within a steady state. The horizontal error bar denotes the estimated catalytic efficiency based on the minimum and the maximum error-bar values of the measured data of $q_D/q_i$ shown in Fig. 20. The data of Park et al. [9] was obtained in an arcjet wind tunnel at total flow enthalpy of 40.6 MJ/kg in air. The vertical error bar in their data was estimated
Fig. 22 Variation of surface catalytic efficiency with wall temperature.

by the author using the typical output trace from a copper-slug calorimeter (Fig. 2 in Park et al.). The data of Anderson [7] were also obtained in an arcjet at total enthalpy varying from 12 MJ/kg to 120 MJ/kg in nitrogen. Because the author could not find a testing detail of Goulard [1] his $\gamma_w$ values are regarded as estimated values. The data of Herdrich et al. [5] represents the literature values of Cu and CuO that were obtained from side-arm reactor facilities mostly at 300 K.

Concerning the CuO-wall data it can be seen that the present catalytic-efficiency value is much lower than others. It is lower by about a factor of 3.5 and 7 compared with Park et al. [9] data and Goulard’s value [1], respectively. Looking at the data of Herdrich et al. [5] their presented literature values are much higher than the present data as well as that of Park et al. [9]. Because these values were obtained from the side-arm facilities in which efficiencies are determined in a very different way, making direct comparisons between the two approaches would be difficult. It is known that the accuracy of the side-arm method deteriorates at high $\gamma_w$ values [2]. Possibly, the $\gamma_w$ values of Cu and CuO are too high for a side-arm method to be efficient.

As mentioned in Sec. VI.B, it seems quite certain that the surface was rough during the experiment of Park et al. [9], so the effective catalytic efficiency is expected to be higher than that in the present case. Also, it is well known that an increase in wall temperature increases the efficiency [1,7,10,12]. In this context the reason for having a much lower efficiency for the present case can be thought to be the consequence of having either a lower wall temperature or a smoother wall, or the combination of the two.

Referring to the Cu-wall data, the present value is again much lower than others. It is lower by about a factor of 11 and 6 compared to the Goulard [1] and Anderson [7] values, respectively. The present value combined with the data of Anderson shows that efficiency increases with an increase in wall temperature. Looking at the data of Park et al. [9] for the Cu wall and the data of Anderson [7] for the CuO wall, it is seen that, at the given wall temperature of $T_w = 450$ K to 500 K the efficiency for Cu is about an order of magnitude higher than that to the CuO. A similar observation can also be made by looking at the present data and Goulard’s estimates.

According to Harthun et al. [36] the oxygen catalytic efficiency of the heat-shield material for the space shuttle varies as $\gamma_w \propto e^{-n/T_w}$ where $n \approx 4028$. If this relationship is applied to the data of Park et al. [9] to extrapolate to 350 K one obtains a predicted $\gamma_w$ value of about 0.0008. This value is significantly lower than the present $\gamma_w$ values of 0.0026 to 0.0032. This difference may be attributable to the difference in surface material used in the space shuttle and in the experiment of Park et al.

VII. Conclusions

In the stagnation-heat-transfer experiment using the shock tube copper surface showed a 28% and 45% higher heat-transfer rate than copper-oxide and silicon-dioxide surfaces, respectively. The copper-oxide value was 9% to 13% higher than that of the silicon-dioxide-coated surfaces. All coated surfaces were examined under a scanning electron microscope before and after the tests to confirm that the surface structure remained intact. A negligible amount of atomic oxygen is absorbed on the surface during the tests. The tertiary-mixture heat-transfer-rate formula obtained in the present work resembles Goulard’s binary formula, but it contains additional variable parameters. When catalytic efficiency is low the present expression agrees with Goulard’s expression. When catalytic efficiency is high the tertiary case predicts a higher heat-transfer rate than Goulard’s formula. Using this theoretical result the catalytic efficiency of copper oxide is deduced to be 0.0026 to 0.0032, whereas copper has an efficiency of 0.016 for a smooth wall.

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