Abstract for Specialists' Meeting AVT-199 /RSM-029 -on Catalytic Gas Surface Interactions

Influence of Catalysis and Oxidation on Slug Calorimeter Measurements in Arc Jets

Anuscheh Nawaz*, Dave Driver**, Imelda Terrazas Salinas***

*Anuscheh Nawaz, Sierra Lobo Inc., Thermophysics Facilities Branch, NASA Ames Research Center, MS 229-4, Moffett Field, CA
**Dave Driver, Reacting Flow Environments Branch, NASA Ames Research Center, MS 230-2, Moffett Field, CA
***Imelda Terrazas Salinas, Thermophysics Facilities Branch, NASA Ames Research Center, MS 229-4, Moffett Field, CA

Introduction and Motivation

Arc jet tests play a critical role in the characterization and certification of thermal protection materials and systems (TPS). The results from these arc jet tests feed directly into computational models of material response and aerothermodynamics to predict the performance of the TPS in flight. Thus the precise knowledge of the plasma environment to which the test material is subjected, is invaluable. As one of the environmental parameters, the heat flux is commonly measured. The measured heat flux is used to determine the plasma enthalpy through analytical or computational models.

At NASA Ames Research Center (ARC), slug calorimeters of a geometrically similar body to the test article are routinely used to determine the heat flux. A slug calorimeter is a thermal capacitance–type calorimeter that uses the temperature rise in a thermally insulated slug to determine the heat transfer rate, see Figure 1(left). Current best practices for measuring the heat flux with a slug calorimeter are described in ASTM E457 – 96 [1]. Both the calorimeter body and slug are made of Oxygen Free High Conductivity Copper, and are cleaned before each run.

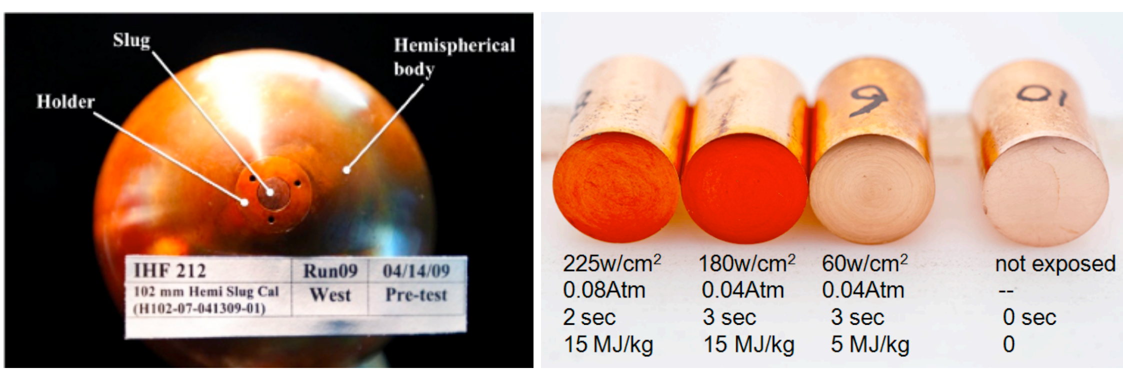

Figure 1 (left) Example of hemispherical slug calorimeter used to determine heat flux. (right) Color change of slugs exposed to different arc jet conditions suggests oxidation of copper.

The enthalpy in plasma can be described as a sum:

$$h_{plasma} = \sum_i c_i \left[\Delta h_{f,i} + h_i(T)\right] + \frac{1}{2}v^2$$

where c_i mass fraction of the species, $\Delta h_{f,i}$ is the standard enthalpy of formation, and v is the velocity of the plasma. The total enthalpy is thus a sum of the chemical enthalpy (dissociation, ionization), the enthalpy related to the temperature of the plasma (rotational, vibrational, translational movement), and the kinetic enthalpy. The catalytic efficiency of the calorimeter surface directly influences the fraction of the chemical enthalpy seen by the sensor. The lower the catalycity, the smaller the fraction registered. In order to determine plasma enthalpy from heat flux measurements it is thus desirable to either have a fully catalytic sensor surface, or to accurately know the catalytic efficiency of the material.

In the recent past, attention has been drawn to the fact that slugs are frequently discolored, pointing to possible surface oxidation, in particular after high enthalpy arc jet runs – see Figure 1 (right).
At high enthalpy conditions, an oxidized slug, with a surface composition of CuO or Cu_2O would have a significant impact on the heat flux measured. From literature, pure copper is nearly fully catalytic ($\gamma \approx 0.1$), where copper oxide falls into the range of medium catalytic efficiency ($\gamma \approx 0.02$)[2]. Thus the heat flux registered, and the enthalpy derived, would be lower for copper oxide than for pure copper when exposed to the same plasma condition. For material tests, the testing environment in the arc jet is adjusted to meet a required enthalpy. This means that test enthalpies determined from oxidized slugs might be higher than required, since a portion of the enthalpy is not reflected in the heat flux. Material samples would thus potentially be tested at conditions that are higher than necessary.

In order to determine the degree to which arc jet heat flux measurements are influenced by catalytic and oxidation effects a systematic study is being conducted. It aims at answering the following questions:

- Does the surface composition on a copper calorimeter change during a measurement?
- How does the surface composition change?
- When and how fast does the surface composition change?
- Does this change affect the heat flux reading and by how much?
- How does this affect the CFD material response predicted?

And, following these questions:
- Can we avoid surface composition changes during a heat flux measurement, in the interest of having a well-defined measurement?
- Can we recommend best practices for future test?

Methodology

The methodology used will be described thoroughly in the full paper. The following aspects are highlighted here:

XPS analysis

X-ray Photon Spectroscopy (XPS) is used to analyze the surface composition of the slugs before and after plasma exposure. Monochromatic x-rays are irradiated onto the sample surface, resulting in the emission of photoelectrons whose energies are characteristic of the elements within the sampling volume. The measurement depth is between 0 and 70Å. This technique can be coupled with ion sputtering, to determine an upper boundary for the depth of composition change. This analysis service was provided by EAG (Evans Analytical Group).

SiO_2 coating of copper slugs

To achieve a low catalytic surface material, while retaining the high conductivity of copper, the copper slug was sputtered with SiO_2. In this technique, the solid SiO_2 source is bombarded with Argon plasma, which cause it to release and deposit molecular SiO_2 onto the strategically placed target material.

Experiment

Tests were performed in the Aerodynamic Heating Facility (AHF) at NASA Ames Research Center with a 46cm diameter nozzle. Calorimeter slugs were systematically exposed to 6MJ/kg, 15MJ/kg and 16 MJ/kg conditions. Post-test analysis was performed using XPS.

The following tests were conducted thus far:

1- Pre-test, aimed at understanding the surface condition before insertion into the plasma

2- AHF 297 Run2, aimed at characterizing the surface of copper slugs after plasma exposure at three conditions. Additionally, a slug was inserted several times to determine the influence of multiple insertions in the same test run. The surface of all slugs was analyzed.

3- AHF 297 Run3, aimed at investigating the difference in heat flux due to other metal surfaces such as Nickel, Gold, Constantan and Platinum. The surface of all materials was analyzed post test.

It is further planned to conduct at least one more test series aimed at understanding the rate at which the copper slug surface oxidizes, as well as investigate the use of other surface materials such as CuO and SiO_2.

Results

The preliminary results from this study show oxidation of copper surfaces to Cu2O before run, and to CuO during plasma exposure, even at low heat flux conditions. Further results will be presented in the full paper. In addition, the impact of the catalytic efficiency on computational models will be explored.

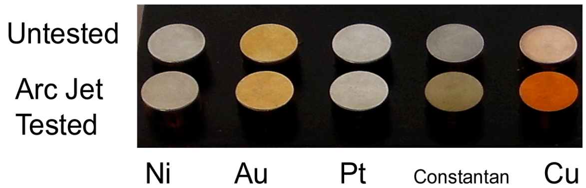

Figure 2 Nickel, Gold, Platinum, Constantan and Copper surfaces pre-and post plasma exposure.

References

[1] ASTM E457-96 (Reapproved 2002) "Standard Test Method for Measuring Heat-Transfer Rate Using a Thermal Capacitance (Slug) Calorimeter."

[2] Cauquot, P. Cavadias, S., Amouroux, J., Thermal Energy Accomodation from Oxygen Atoms Recombination on Metallic Surfaces, Journal of Thermophysics and Heat Transfer, Vol.12, No.2, April- June 1998

Research and Technology Agency
BP 25 – 92201 Neuilly-sur-Seine

Applied Vehicle Technology Panel
Tel: + 33 1 55 61 22 87 /85 – Fax + 33 1 55 61 22 98/99
e-mail: cheynes@rta.nato.int

Preliminary Meeting Announcement and

CALL FOR PAPERS

Specialists' Meeting AVT-199 /RSM-029 -on

Catalytic Gas Surface Interactions

organized by the Members of the

APPLIED VEHICLE TECHNOLOGY PANEL (AVT)

AVT-199 Programme Committee

to be held at the von Karman Institute, Rhode-St-Genese, Belgium

22-24 October 2012

Contributions and participation are invited from NATO Nations, Japan, Russia and Switzerland

Note: Final date for submission of abstract 15 March 2012

For further details, please consult the following sections regarding
General Scope of the Meeting
Deadlines and Schedule
Procedures
AVT-199 Programme Committee
Abstract Submission Form

General Scope of the Meeting

The Applied Vehicle Technology Panel (AVT) of the Research and Technology Organization (RTO) of NATO is organizing a Specialists' Meeting entitled "Catalytic Gas Surface Interactions". The meeting will be open to NATO Nations, Japan, Russia and Switzerland and is to be held at the von Karman Institute for Fluid Dynamics in Rhode-St-Genese, Belgium from 22-24 October, 2012.

The primary objective of this meeting is to develop a coordinated international activity aimed at providing experimental data on gas-surface interactions that can be used to validate numerical models of these processes. The outcome of this meeting will be a roadmap that will define a framework for complementary studies yielding data for a particular surface-catalyzed reaction, based on the strengths of the different participating groups. All aspects of such a study will be addressed, including plasma test facilities, instrumentation, materials, plasma composition, and relevance to NATO missions.

Discussion sessions during the meeting will facilitate discussions between modelers and experimentalists to design a set of coordinated experiments that address all aspects of the coordinated study. Recognizing the overarching limitation of available research funding, discussions will consider existing data and minimum cost efforts to either supplement such data or provide improved measurements. All researchers within this community, from national laboratories, universities, and industry are welcome to participate. Papers from all groups that address these topics are welcome.

Gas-surface interactions such as surface catalysis significantly impact surface heating for both internal and external flows. Catalyzed surface reactions are driven by flow chemistry, and so are of particular importance in the development of hypersonic vehicles, where shock-induced dissociation can lead to significant, non-equilibrium atomic fluxes impinging on wetted surfaces. Moreover, the current use of limiting assumptions rather than physics based models of gas-surface boundary conditions for predicting vehicle or component performance using computational models has been identified as a limitation for current component design tools. Considering that for external flows, surface catalyzed reactions can augment the heat flux by up to a factor of two, the importance of developing better gas-surface interaction models is clear. Experimental data are needed to better characterize gas-surface interactions and thereby inform the development of higher fidelity surface chemistry models. Such data can be acquired using advanced optical diagnostic techniques in plasma test facilities, but no facility has access to all diagnostic techniques. A major objective of this meeting is, therefore, to develop a road map for a coordinated international effort aimed at providing complementary data that can be used to characterize one or more surface-catalyzed reactions for a relevant material/plasma configuration.

Key topics include: 1) gas-surface interaction modeling: 2) ground test facilities and spectroscopic instrumentation capabilities; 3) pre- and post-test material characterization; 4) candidate gas-surface interaction systems for investigation including material source and purity; 5) preliminary surface-catalyzed recombination measurement results; 6) other relevant topics.

Deadlines and Schedule

1 February 2012	**Distribution of Call for Papers** to solicit abstracts from NATO Nations, Japan, Russia and Switzerland after: authors to send their abstracts to the Programme Committee (see procedures)
15 March 2012	**Abstract Submission deadline** after: Programme Committee to create the Specialists' Meeting Programme from received abstracts
9 April 2012	**Authors informed of Selection Decision** Programme Committee to inform selected as well as rejected authors. RTA to dispatch authors' information package to selected authors after: selected authors to prepare their papers, presentation and clearances
20 April 2012	**Final Agenda Approved by Programme Committee** Programme Committee to finalise the Programme after: RTA to prepare and publish the official Meeting Announcement
8 June 2012	**Submission of Advanced copy of US papers to US National Coordinator** Deadline for US authors to submit their copy of their advance paper to the US National Coordinator (special instructions to be issued with author's information package
17 August 2012	**Electronic Advance Copy of Paper due at RTA** deadline for all authors to send an advance copy of their full paper to RTA after: the Technical Evaluator for the Specialists' Meeting to review all submitted papers
14 September 2012	**Submission of Final Version of all Papers to RTA** deadline for all authors to send their final papers to RTA after: RTA to pre-release all papers on the RTO website making them accessible to all registered participants to the Specialists' Meeting Note that no paper copies will be available at the meeting site
20-24 October 2012	**Specialists' Meeting held at von Karman Institute, Rhode-St-Genese, Belgium**
15 November 2012	**Submission of Corrected Manuscripts** deadline for all papers to be included in the Meeting Proceedings after: RTA to edit, prepare, produce Meeting Proceedings which will be made accessible through the RTO website

Procedures

Security Level and Clearance for Presentation

The Specialists' Meeting classified as "NATO UNCLASSIFIED + Japan, Russia and Switzerland (open to citizens of NATO Nations, Japan, Russia and Switzerland only). The distribution of the papers will be NATO UNCLASSIFIED + Japan, Russia and Switzerland. For the full overview of NATO Nations please consult the section on NATO Nations Overview.

It is the responsibility of each contributor to fulfil the publication release requirements of his/her organization/company and country and to obtain clearance of abstracts and full papers as needed. An official clearance is mandatory in the United States and there may also be a requirement in other countries to obtain clearance for unclassified abstracts and full papers. For further information, authors should consult the appropriate **Programme Committee Member** listed in this document or the Co-Chairs.

Invitation and Format of Abstracts

- The initial abstract should describe (in 1000 to 1500 words), the aim, results and conclusions of the work. Inclusion of 1 to 2 figures and/or photographs to support the abstract is encouraged. All abstracts should be submitted by **e-mail** to the **Programme Committee Co-Chairs** identified below.

- The full paper (approximately 12 pages) will be requested once the Programme Committee has developed the final agenda for the Symposium.

- Both the abstracts and the full paper must also contain a declaration from the author(s) that there are no restrictions regarding presentation neither during the Symposium nor of the publication in the Meeting Proceedings. Authors' names, complete mailing addresses and other requested information must be included with the abstracts. Please use the **Abstract Submittal Form (Attachment 1)** and keep the size of files less than 2 MB.

Programme Committee Co-Chairs

Prof. Douglas G. Fletcher
douglas.fletcher@uvm.edu

Dr. Georg Herdrich
herdrich@irs.uni-stuttgart.de

Prof. T. Schwartzentruber
schwartz@aem.umn.edu

Paper Preparation and Procedure

Authors of papers selected for presentation and publication will be notified by the Programme Committee. The AVT Executive office at RTA will then send detailed instructions concerning the preparation of manuscripts to lead authors. Questions related to technical aspects of the program or the papers should be addressed to the Technical Committee Chairmen as indicated above. Questions of an administrative nature should be addressed to the AVT Executive Office

RTA/AVT Executive Office
Attn: Sandra Cheyne
BP 25
92201 Neuilly sur Seine – Cedex, France
Tel : +33 1 55 61 22 87
e-mail : cheynes@rta.nato.int

The special procedure for papers submitted by US authors will be explained in the author's package.

The NATO RESEARCH AND TECHNOLOGY ORGANISATION

The NATO RESEARCH AND TECHNOLOGY ORGANISATION (RTO) promotes and conducts co-operative scientific research and exchange of technical information amongst NATO nations and NATO partners. The largest such collaborative body in the world, the RTO encompasses over 3000 scientists and engineers addressing the complete scope of defence technologies and operational domains. This effort is supported by an executive agency, the Research and Technology Agency (RTA), which facilitates the collaboration by organising a wide range of studies, workshops, symposia, and other forums in which researchers can meet and exchange knowledge.

For further information, please consult the RTO web site.

Representing one of the technical domains within RTO, the APPLIED VEHICLE TECHNOLOGY PANEL (AVT) strives to improve the performance, affordability, and safety of vehicles through the advancement of appropriate technologies. The Panel addresses vehicle platforms, propulsion and power systems operating in all environments (land, sea, air, and space), for both new and ageing systems.

Further details are given on the AVT web site:

The RTO and AVT websites provide a wide variety of information and on-line services ranging from overview information on the organization's mission to news regarding upcoming events. You will find on-line access to more than 300 scientific publications as well as information on current activities.

For further assistance do not hesitate to contact the AVT Executive Office

AVT-199 PROGRAMME COMMITTEE

Co Chairs

Prof. Douglas G. Fletcher
University of Vermont
Mechanical Engineering
201 Votey Hall, 33 Colchester Ave
Burlington VT 05405, United States
email: douglas.fletcher@uvm.edu

Dr. G. Herdrich
Institute of Space Systems (IRS)
University of Stuttgart, Pfaffenwaldring 31
70569 Stuttgart, Germany
email: herdrich@irs.uni-stuttgart.de

Prof. T. Schwartzentruber
University of Minnesota
110 Union St. SE, Minneapolis, MN 55455
United States
email: schwartz@aem.umn.edu

Members

Belgium
Assoc. Prof. O. Chazot
VKI
Chaussee de Waterloo, 72
B-1640 Rhode St Genese
email: Chazot@vki.ac.be

France
Mme M. Balat-Pichelin
Laboratoire Procedes
Materiaux et Energie Solaire
PROMES-SNRS
UPR 8521, rue du four solaire
66120 Fort Romeu Odeillo
balat@promes.cnrs.fr

Mr. F. Sourgen
ONERA
BP 74025 - 2 avenue Edouard Belin,
31055 TOULOUSE cedex 4
email: Frederic.sourgen@onera.fr

Mr. J-L. Verant
ONERA
2, avenue E. Belin
31055 Toulouse Cedex
email: verant@onecert.fr

Germany
Dr-Ing. M.K. Fertig
German Aerospace Center
Lilienthalplatz 7
D-38108 Braunschweig
email: markus.gertig@dlr.de

Dr. Ing. A. Guelhan
German Aerospace Center
Linder Hoehe
D-51147 Cologne
email: ali.guelhan@dlr.de

Italy
Prof. C. Bruno
Universita degli Studi di Roma
La Sapienza, Dipartimento Meccanica
Aeronautica
Via Eudossiana, 18, 00184 ROMA
email: cbruno@dma.ing.uniroma1.it

Mr. M. Capitelli
Universita di Bari
Dept. of Chemistry
Campus Universitario
70124 Bari
email: mario.capitelli@ba.imip.cnr.it

The Netherlands
Dipl.-Ing. J. Thoemel
ESA/AOES
Keplerlaan 1
2001 AZ Noordwijk
email: jan.thoemel@esa.int

Dr. L. Walpot
AOES Group-B.V.
Haagse Schouwweg 6G
2332 KG Leiden
email: lwalpot@aoes.com

United States
Dr. D. Bose
NASA Ames Research Center
MS: 230-3, NASA Ames Res. Ctr.,
Moffett Field, CA 94035,
email: dbose@mail.arc.nasa.gov

Prof. I. Boyd
University of Michigan
Department of Aerospace Engineering
1320 Beal Avenue,
Ann Arbor MI 48109-2140
email: ianboyd@umich.edu

Dr. M. Maclean
CUBRC
LENS Aerosciences
4455 Genesee Street
Buffalo, NY 14225
email: maclean@cubrc.org

Mr. J. Marschall
SRI International
Molecular Physics Laboratory,
333 Ravenswood Avenue
Menlo Park, CA 94025
email: jochen.marchall@sri.com

OVERVIEW OF NATO NATIONS

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* Iceland and Luxembourg are NATO members, but currently do not participate in the RTO framework.

Attachment 1

AVT ABSTRACT SUBMISSION FORM

SUBJECT: AVT-199/RSM-029 Catalytic Gas Surface Interactions

(NATO Unclassified+Japan+Russia+Switzerland = releasable to these Nations only)

Authors/co-authors listed in the order they will appear on final manuscript with forenames or initials, and titles, e.g. Dr., Prof., etc.

1. Title Name Nationality ____

Affiliation**:** ____

Full Mailing Address: ____

____

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Name of submitting author and date of submission