Applied Surface Science 316 (2014) 385–397

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Air plasma-material interactions at the oxidized surface of the PM1000 nickel-chromium superalloy

Francesco Panerai [a,*,1], Jochen Marschall [b], Jan Thömel [a], Isabelle Vandendael [c], Annick Hubin [c], Olivier Chazot [a]

[a] Aeronautics and Aerospace Department, von Karman Institute for Fluid Dynamics, Chaussée de Waterloo 72, 1640 Rhode-Saint-Genèse, Belgium
[b] Molecular Physics Program, SRI International, 333 Ravenswood Avenue, Menlo Park, CA 94025, USA
[c] Department of Materials and Chemistry, Research Group of Electrochemical and Surface Engineering, Vrije Universiteit Brussel, Pleinlaan 2, B-1050 Brussels, Belgium

ARTICLE INFO

Article history:
Received 2 June 2014
Received in revised form 25 July 2014
Accepted 3 August 2014
Available online 9 August 2014

Keywords:
Oxidation
Nickel based superalloys
Thermal protection system

ABSTRACT

Nickel-based superalloys are promising options for the thermal protection systems of hypersonic re-entry vehicles operating under moderate aerothermal heating conditions. We present an experimental study on the interactions between PM1000, an oxide dispersion strengthened nickel-chromium superalloy, and air plasma at surface temperatures between 1000 and 1600 K and pressures of 1500, 7500 and 10,000 Pa. Pre-oxidized PM1000 specimens are tested in high-enthalpy reactive air plasma flows generated by the Plasmatron wind tunnel at the von Karman Institute for Fluid Dynamics. Microscopic analysis of plasma-exposed specimens shows enhanced damage to the chromia scale at the lowest plasma pressure. Elemental surface analysis reveals the loss of Cr and the enhancement of Ni at the scale surface. A thermodynamic analysis supports the accelerated volatilization of Cr_2O_3 and the relative stability of NiO in the presence of atomic oxygen. Changes in the reflectance and emissivity of the oxidized surfaces due to plasma-exposure are presented. The catalytic efficiencies for dissociated air species recombination are determined as a function of surface temperature and pressure through a numerical rebuilding procedure and are compared with values presented in the literature for the same material.

1. Introduction

Reusable hypersonic vehicles re-entering the Earth's atmosphere must be protected by a thermal protection system (TPS) in order to survive the harsh aerothermal environment. Nickel-chromium-based superalloys are promising thermal protection materials (TPMs) for surfaces or components that operate below 1600 K. Their ability to form compact, protective oxide layers and their self-healing properties in reactive environments make them an appealing choice. Furthermore, their ductility and design flexibility offer the potential for robust systems with low maintenance costs. Several investigations and applications can be found in the literature on metallic TPSs [1–7].

An oxide dispersion strengthened (ODS) Ni–Cr superalloy, PM1000, has been investigated in the framework of the EXPERT mission of the European Space Agency as a TPM for the body skirt of the EXPERT capsule [8]. PM1000 contains (by mass) ~20% Cr, ~3% Fe, and less than 1% Al, Ti, and Y_2O_3, with the balance Ni [1]. Between 900 °C and 1100 °C, PM1000 oxidizes in equilibrium air to form a compact Cr_2O_3 oxide scale with minor amounts of NiO and $NiCr_2O_4$, and even smaller amounts of Al_2O_3 and TiO_2 [9]. The EXPERT mission was designed to be a test bed for investigating aerothermodynamics phenomena. The use of PM1000 on the EXPERT capsule aimed to enhance the understanding of metallic TPM performance in reactive re-entry environments and to elevate the technology readiness level of metal-based TPSs.

Because metallic TPS materials oxidize at high temperatures, the formation, transformation, and stability of surface oxide scales in aerothermal re-entry environments are of key importance. Self-limiting (passive) oxidation requires a thermochemically-stable, dense oxide scale that acts as an efficient barrier to the diffusion of oxygen inward and metal constituents outward. The surface properties of the oxide scale – in particular, the emissivity and the catalytic efficiency – have a large impact on the peak heating and integrated heat load experience by the TPS, since the emissivity dictates the ability of the TPS to reject heat by radiation

* Corresponding author. Tel.: +32 2 359 96 11; fax: +32 2 359 96 00.
E-mail addresses: panerai@vki.ac.be, francesco.panerai@uky.edu (F. Panerai).
[1] Current address: Department of Mechanical Engineering, University of Kentucky, 151 Ralph G. Anderson Building, Lexington, KY 40506, USA.

http://dx.doi.org/10.1016/j.apsusc.2014.08.017
0169-4332/

and the catalytic efficiency determines the level of heating caused by heterogeneous recombination reactions involving oxygen and nitrogen atoms. The gases impinging on the TPS in flight can be highly dissociated and in chemical non-equilibrium at the temperature of the TPS surface. Therefore, furnace tests under thermochemical equilibrium conditions are not representative of the reactive air plasma flows encountered by hypersonic vehicles. Only a limited amount of information is so far available on the properties and performance of oxidized PM1000 in dissociated flows.

Pre-oxidized specimens of PM1000 have been exposed to laboratory plasmas generated by microwave discharge systems by Balat-Pichelin and Bêche [1] and Stewart and Bouslog [5]. The primary purpose of these investigations was to extract surface catalytic properties as a function of temperature, by measuring and modeling atom concentration gradients near specimen surfaces. Balat-Pichelin and Bêche [1] determined atomic oxygen recombination coefficients in air using a flow-tube reactor at total pressures of 300 and 1000 Pa and surface temperatures between 850 and 1650 K. Stewart and Bouslog [5] measured O-atom and N-atom recombination coefficients in a diffusion-tube side-arm reactor in partially-dissociated oxygen and nitrogen, respectively. Measurements were conducted at 36 Pa total pressure in the temperature range 300–1200 K. In these laboratory test environments, oxygen dissociation fractions in the test section are generally lower than those found in the free stream of a high enthalpy plasma facility. The density of O-atoms near the test specimen surface depends on the proximity of the specimen to the microwave cavity and the flow conditions in the reactor. Balat and Vesel [10] estimated an oxygen dissociation degree of ~70% in microwave air plasma at conditions (4 l/h flow) similar to those applied during the PM1000 study in [1]. Vesel et al. [11] showed that in microwave oxygen plasma the degree of dissociation is ~12% compared to the reported ~70% for air plasma under the same experimental conditions.

Several researchers have subjected PM1000 specimens to high enthalpy flows using inductively-coupled plasma (ICP) or arc-jet facilities, where under most relevant operating conditions oxygen is fully-dissociated in the free stream. Stewart [7] and Stewart and Bouslog [5] performed arc-jet-tests in panel and stagnation point configurations on pre-oxidized PM1000 specimens and investigated the stability of oxide scales, as well as the radiative and catalytic properties of plasma-exposed surfaces. Stagnation point pressures ranged from 500 to 3550 Pa and surface temperatures between 1200 and 1730 K. Schüßler et al. [3] exposed virgin PM1000 specimens to pure oxygen at 40 Pa in an ICP facility and determined oxygen recombination coefficients using an experimental/numerical procedure based on Goulard theory and inverse heat flux calculations. They compared their results with previous measurements by Pidan using an analogous approach [12]. Schüßler et al. [3] also measured the total normal emissivities of virgin and plasma-oxidized PM1000 between 600 and 1600 K using a blackbody cavity. De Heij et al. [13] and Sudmeijer et al. [14] performed microscopic analyses of PM1000 samples exposed to induction-generated air plasma, at surface temperatures between 1173 and 1573 K. They showed that the cohesion and uniformity of chromia scales at PM1000 surfaces are severely degraded by plasma exposure. Sudmeijer et al. [14] documented that the mass loss of Cr from the surface scale increases at higher temperatures and lower pressures.

The present study aims at characterizing the gas/material interactions (catalysis, re-radiation and oxidation) at the oxidized PM1000 surface in air plasma. We describe an experimental campaign conducted at the Plasmatron facility at the von Karman Institute for Fluid Dynamics (VKI). The work includes higher pressure conditions than some of the previous testing [1,3,5,7] in order to reproduce lower altitude flight conditions. The plasma flow is characterized using calorimetric and Pitot measurements, while infrared techniques are applied to determine the surface temperature of the samples while they are exposed to plasma. In distinction to previous PM1000 investigations in high enthalpy flows, here we attempt to model the gas composition interacting with the surface during the tests. To this aim a non-equilibrium boundary layer solver is used to numerically rebuild the gas conditions in front of the test specimen and a thermodynamic volatilization model is used to rationalize observed trends as a function of temperature and O-atom pressure. Microscopic analyses of the samples are performed to evaluate changes in the oxide scale morphology and composition due to plasma exposure. The room temperature reflectivities of the pre-oxidized and plasma-tested materials are measured and are used to compute their total hemispherical emissivities. Catalytic recombination efficiencies are extracted from the boundary layer solver and are discussed in comparison to published measurements by other investigators.

2. Experiment

2.1. Setup and instrumentation

Current state-of-the-art aerothermodynamics ground testing relies on decoupling high speed and high temperature effects in two classes of facilities. The first reproduces flight Mach and Reynolds numbers in short duration experiments, while the second simulates thermal and chemical phenomena, during a test time long enough to obtain significant heat loads to assess the performance of TPS in flight-like conditions. The Plasmatron facility at VKI belongs to this second class. The connection between the Plasmatron test environment and the re-entry environment relies on the local heat transfer simulation (LHTS) methodology [15,16]. If the hypersonic (re-entry vehicle) and subsonic (Plasmatron) boundary layers edge conditions are close to thermochemical equilibrium, then the stagnation point heat transfer to the test model is the same as that in flight, under the conditions that flight and ground total enthalpy, total pressure and velocity gradient are equivalent. To duplicate the flight boundary layer chemistry, the Plasmatron produces a subsonic plasma jet by electromagnetic induction, into a test chamber at sub-atmospheric pressure. The inductively-coupled plasma (ICP) generation provides an impurities-free flow that is ideal for studying the gas/surface interactions of a TPM in a simulated re-entry environment. The reader is referred to [17] for further details about the Plasmatron facility.

In the present measurements we use two different specimen geometries and model holder configurations, as shown in Fig. 1. The standard (ST) configuration is a 26.6 mm diameter, 3 mm thick specimen mounted in 50 mm diameter model holder with 10 mm corner radius. The equilibrium (EQ) configuration is a 90.0 mm

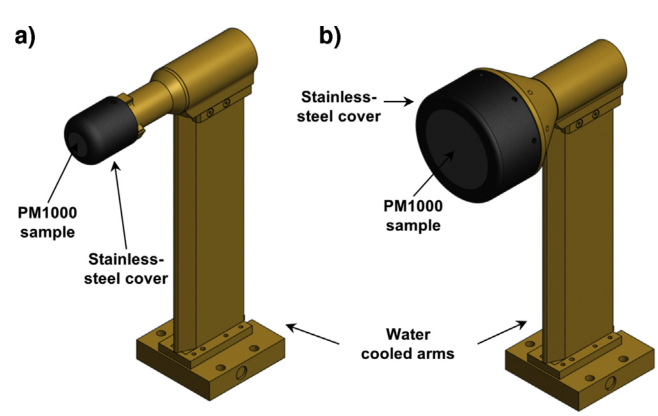

Fig. 1. Plasmatron test probes and model holder configurations: (a) standard (ST) and (b) equilibrium (EQ).