Thermal Stress Analysis of Ceramic Pellets for Catalysis

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One of the most critical phenomena that limits the lifetime of ceramic catalysts for H_2O_2 decomposition is represented by substrate break-up as a consequence of thermal shocking. In a recent experimental campaign conducted by Alta S.p.A., Pisa, Italy, fracture of the ceramic support occurred in a Pt/γ–Al$_2$O$_3$ catalytic bed. Because of the catalyst rupture, the onset of a number of flow instabilities and the marked increase of the pressure drop in the decomposition bed led to a severe decrease of the engine thrust. In order to take proper action for enhancing the thermal shock resistance of the catalyst bed it has been necessary to better understand the dynamics of the heat transfer between the decomposing propellant and the catalyst support. In this work a reduced order model of the thermal transient and the associated thermal stresses in the catalyst pellets is presented. The indications provided by the model have therefore been used for orienting the selection of a suitable catalyst carrier and the development of a new Pt/α–Al$_2$O$_3$ catalyst, here indicated as LR-III-127. Its strength and propulsive performance have been experimentally evaluated under realistic working conditions in a HTP thruster prototype. After the decomposition of 1.5 kg of H_2O_2 (90% by weight) the LR-III-127 catalyst displayed a low susceptibility to thermal cracking and outstanding performance in terms of decomposition efficiency.

Nomenclature

A_t	=	throat area
C_F	=	thrust coefficient
c^*	=	characteristic velocity
F	=	thrust
g_o	=	sea level gravity acceleration
I_{sp}	=	specific impulse
$\dot{m}$	=	propellant mass flow rate
p_a	=	ambient pressure
p_c	=	combustion chamber pressure
R	=	gas constant of the exhaust gases
T_{ad}	=	adiabatic decomposition temperature
T_{amb}	=	ambient temperature
T_c	=	combustion chamber temperature

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T_{exp} =   decomposition temperature (experimentally measured)

γ =   specific heat ratio of the exhaust gases

η_{c^*} =   characteristic velocity efficiency

$\eta_{\Delta T}$ =   temperature efficiency

R =   pellet radius

k =   thermal conductivity

α =   thermal diffusivity

h =   heat convective coefficient

T_i =   initial temperature

T_d =   decomposition temperature

α_T =   thermal expansion coefficient

σ_r =   radial stress

σ_ϑ =   tangential stress

σ_φ =   azimuthal stress

λ_j =   eigenvalue

E =   Young module

v =   Poisson ratio

I. Introduction

During the experimentation of a 5N monopropellant thruster working with hydrogen peroxide (HTP) at high concentration (87.5% in mass) some problems associated with the catalytic bed have occurred. The catalyst was prepared by impregnation of γ−Alumina ceramic spheres with a suitable platinum precursor. Fracture of the pellets, and the consequent occlusion of the catalytic bed, have been experienced after sustained operation in the thruster prototype.

Two different fracture modes have been identified in previous experiments: pellet rupture in two nearly equal parts when exposed to lower concentration hydrogen peroxide solutions, and surface chipping in minute fragments (powdering) during the decoposition of HTP. Several flow instabilities and a marked increase of pressure drop across the catalytic bed occurred as a consequence of the catalyst rupture, and quickly led to severe degradation of the engine thrust[1]. The causes of these problems have been identified in several physical phenomena[2,3].

Thermal shocking generated by the impulsive and probably intermittent exposure to the decomposition temperature of hydrogen peroxide is thought to be the main reason for the break-up of the alumina pellets. Out-gassing may also have been a second contributing factor. As liquid peroxide enters the pores of the catalyst support, it is rapidly decomposed and the gaseous reaction products might generate strong overpressures in the porous structure of alumina. As a result, Al_2O_3 pellets can be split or reduced to powder.

A reduced order model of the thermal transient and the induced thermal stresses inside the pellets has been generated in support of the ongoing development of HTP catalytic beds, with the aim of better understanding the problem and addressing the selection of the catalyst substrate towards materials with the necessary mechanical properties. The model is based on the application of the classical 1D solutions for the unsteady heat conduction equation and the linear static elasticity theory of thermal stresses for spherical pellets. The separable closed form solution of the heat conduction equation is expressed by an infinite series, which depends on the boundary conditions imposed at the pellet surface. Conservatively, an impulsive stepwise change of the surface temperature from room conditions to the HTP adiabatic decomposition temperature (corresponding to an infinite value of the

heat transfer coefficient) has been assumed, and the ensuing thermal field has been used as input to the second equation for evaluating the thermal stresses in the pellets. The model results indicated the existence of two different mechanisms of pellet break-up, depending on the intensity of the heat release (HTP decomposition rate) at the surface. The model also indicated the need for carriers with higher thermal shock resistance, which can be obtained by:

- reducing the product of the thermal expansion coefficient times the Young's modulus of the support material;
- increasing the ultimate stress of the supporting material;
- increasing the thermal conductivity of the carrier;
- reducing the pellet size.

According to the model results, corundum (α−alumina), cordierite, zirconia and silicon carbide (carborundum) resulted to be potential candidates to substitute γ−alumina as catalyst carrier. Further confirmation of the high thermal shock resistance of zirconia and α−alumina was obtained from drop tests conducted on different catalyst carriers using HTP[4]. A novel catalyst, named LR-III-127, has therefore been produced using the same impregnation technique illustrated by the authors in a previous publication[1]. In order to improve the thermal shock resistance of the catalyst support, granules of compact alpha-alumina with an average size of 100 μm have been chosen as substrate. In this way the ultimate stress of the carrier and typical dimension have been simultaneously modified as indicated by the model. The LR-III-127 catalyst has then been tested in a 5N monopropellant thruster prototype in order to assess the strength of the new carrier under realistic operational conditions. No rupture for thermal shocking was experienced by the catalyst after the decomposition of 2 kg of 90% hydrogen peroxide. The experimental validation of model indications allowed for significant progress to be made in the development of a new and more effective catalyst for H_2O_2 decomposition.

II. Physical Model

The unsteady temperature distribution and the thermal stresses in the spherical pellets have been estimated by introducing the following assumptions:

- pellet radius R, thermal conductivity k and diffusivity α, thermal expansion coefficient α_T, thermal expansion coefficient α_T, Young's modulus E, Poisson modulus ν

- 1D spherically symmetric time-dependent temperature distribution $T(r,t)$

- uniform initial temperature T_i

- convective boundary conditions at the pellet surface with heat transfer coefficient h with the external fluid at the adiabatic decomposition temperature T_d

- spherically symmetric stress field, radial stress σ_r, tangential stresses σ_t

The separable solution of the unsteady heat conduction equation in spherical coordinates:

$$\frac{1}{\alpha}\frac{\partial T}{\partial t} = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial T}{\partial r}\right)$$

with IC and BCs:

$$T(r,0) = T \quad \text{and} \quad -k\left.\frac{\partial T}{\partial r}\right|_{r=R} = h\left(T|_{r=R} - T_d\right)$$

is:

$$T - T_d = 4(T_i - T_d)\sum_{j=1}^{+\infty}\frac{\left[\sin(\lambda_j R) - \lambda_j R\cos(\lambda_j R)\right]}{2\lambda_j R - \sin(2\lambda_j R)}\frac{\sin(\lambda_j r)}{\lambda_j r}e^{-\lambda_j^2\alpha t} \tag{1}$$

where the eigenvalues λ_j are defined by the implicit equation:

$$\tan\lambda_j R = \frac{\lambda_j R}{1 - hR/k} \qquad \text{for} \quad j = 1,2,... \tag{2}$$

By standard methods, the radial and tangential components of the thermal stresses induced in the spherical pellets are expressed by:

$$\sigma_r = \frac{2}{1-\nu} E\alpha_T \left[\frac{1}{R^3} \int_0^R (T - T_i) r'^2 dr' - \frac{1}{r^3} \int_0^r (T - T_i) r'^2 dr' \right] \tag{3}$$

$$\sigma_t = \frac{1}{2r} \frac{d}{dr} \left(\sigma_r r^2 \right) = \frac{1}{1-\nu} E\alpha_T \frac{1}{r} \frac{d}{dr} \left[\frac{r^2}{R^3} \int_0^R (T - T_i) r'^2 dr' - \frac{1}{r} \int_0^r (T - T_i) r'^2 dr' \right] =$$

$$= \frac{1}{1-\nu} E\alpha_T \frac{1}{r} \left[\frac{2r}{R^3} \int_0^R (T - T_i) r'^2 dr' + \frac{1}{r^2} \int_0^r (T - T_i) r'^2 dr' - r(T - T_i) \right] \tag{4}$$

In order to by-pas the difficulty of estimating the actual convective coefficient for the heat exchange between the ceramic pellets and the reacting hydrogen peroxide, the solution coresponding to an impulsive stepwise change of the temperature on the surface of the sphere ($h \rightarrow \infty$) has been conservatively chosen for the approximate evaluation of the transient thermal stresses in the pellets. Table 1 provides the numerical values used for the calculation of the thermal transient and the thermal stresses inside the pellet.

Table 1. Data for the thermal transient analysis

	Value
Initial temperature (T_i)	300 [K]
Decomposition temperature: (T_d)	520 [K] or 950 [K]
Radius of the pellet (R)	0.3 [mm]
Thermal diffusivity (α)	1.023 10^{-5} [m^2/s]
Thermal expansion coefficient (k)	8.4 10^{-6}[1/K]
Poisson's ratio (ν)	0.22
Modulus of elasticity (E)	300 [GPa]
Tensile Strength, Ultimate	200 [MPa]
Compressive Yield Strength	2400 [MPa]

Two values for the decomposition temperature have been used corresponding to the ideal decomposition temperature of a 70 % and 87.5% H_2O_2 solutions. Figure 1 and Figure 2 report the profiles of radial and tangential stresses as functions of the radial distance and time during the decomposition of the 87.5% H_2O_2 solution.
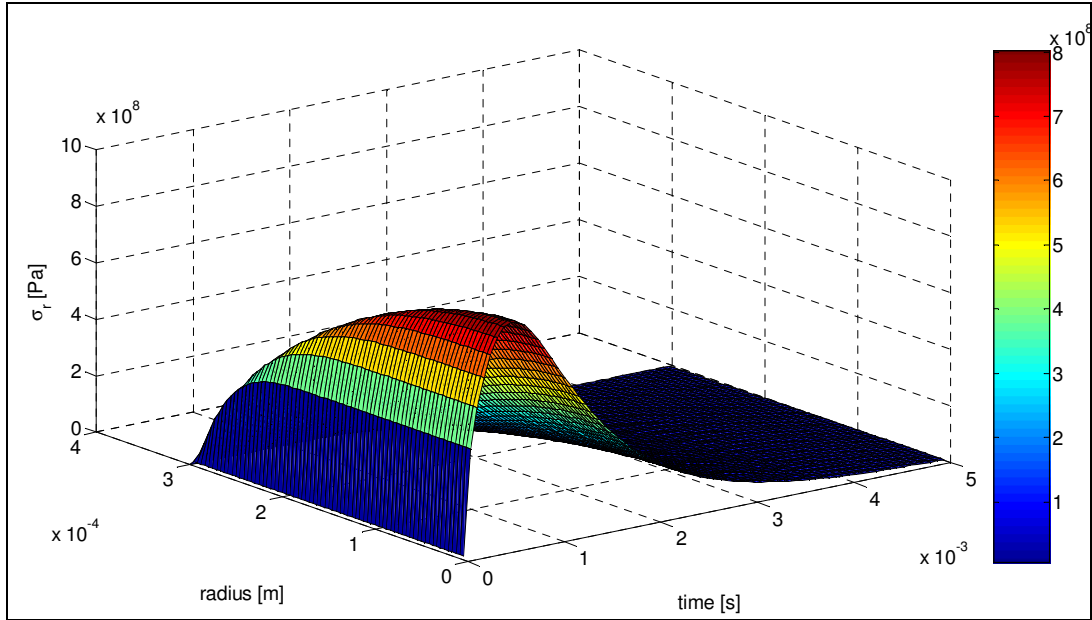

Figure 1. Radial stress (R=0.3 mm; 87.5% H_2O_2)

The main results obtained from the model for two different H_2O_2 concentrations are summarized in Table 2. In detail, the maximum and minimum thermal stresses experienced on the pellet surface and in the core have been

respectively reported. For the expected values of $T_d - T_i$ the thermal stresses at the external surface and at the center of the pellets should be verified as functions of time against the admissible tensions of the catalyst support using a criterion suitable for brittle ceramic materials with asymmetric ultimate compression and tension stresses. The ultimate compression and tension stresses of alumina-based materials are typically -2400 MPa and 200 MPa respectively. As shown in Table 2 is clear that the break-up of ceramic pellets occurs because the maximum radial and tangential stresses exceed the tensile limits of the material. In addition, the amplitude of maximum stresses depends on the temperature difference $T_d - T_i$, and clearly for sufficiently low concentrations of peroxide the material limits are not exceeded.

Table 2. Maximum and minimum thermal stresses

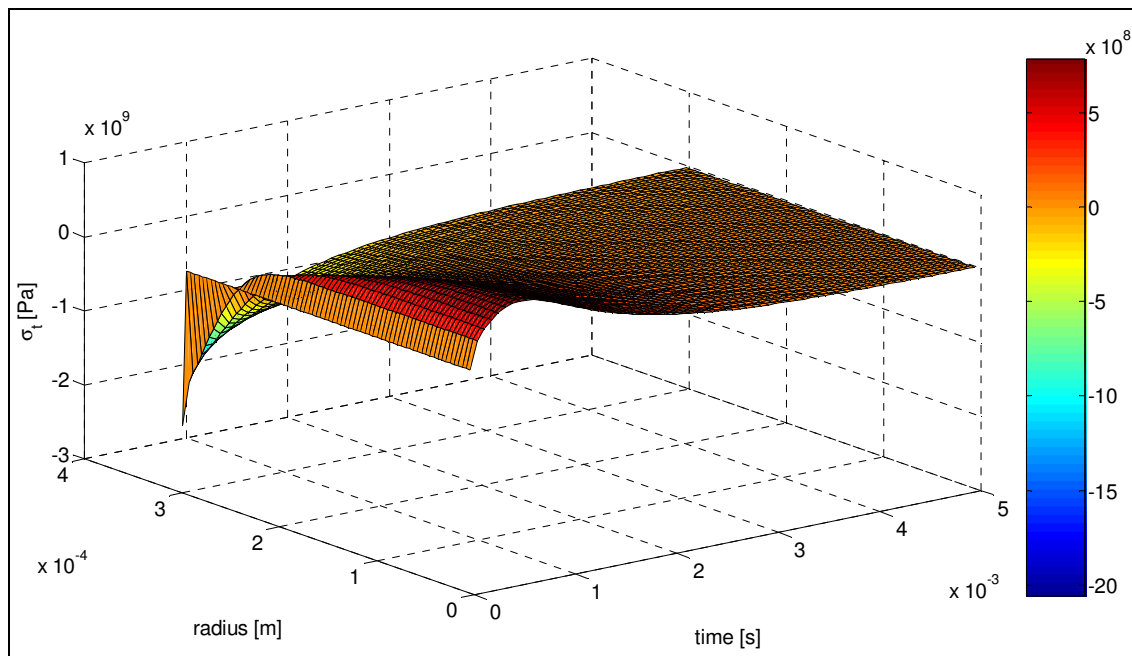| H_2O_2 concentration	70 %		87.5%	
Location	Surface ($r = 0.3$ mm)	Center ($r = 0$ mm)	Surface ($r = 0.3$ mm)	Center ($r = 0$ mm)
$\sigma_{r,max}$	0	275 MPa	0	800 MPa
$\sigma_{r,min}$	0	0	0	0
$\sigma_{t,max}$	0	275 MPa	0	800 MPa
$\sigma_{t,min}$	-750 MPa	0	-2100 MPa	0

Figure 2. Tangential stresses (R = 0.3 mm; 87.5% H_2O_2)

The results indicate that for moderate values of $T_d - T_i$ pellet splitting occurs because the compression stresses initially generated in the outer shell of the pellet do not exceed the limits of the material and the penetration of the thermal wave progressively concentrates tensile stresses on a smaller and smaller inner region, until rupture due to excessive tension stress occurs near the pellet centre and propagates outwards. Conversely, for higher values of $T_d - T_i$ chipping of the pellet surface (powdering) is expected to occur because the compression stresses initially generated in the outer shell of the pellet exceed the limits of the material before the penetration of the thermal wave has time to propagate and induce dangerous tensile stresses in the inner region.

It should be pointed out that the above solution with an impulsive temperature change of the pellet surface is in favor of stability, and yields realistic results only for large values of the pellet's Biot number. Conversely, when, more realistically, the Biot number is reduced to finite values, heat conduction becomes more efficient equalizing the temperature distribution and reducing the thermal stresses.

The analysis indicates that the risk of pellet break-up can be effectively reduced by:

- decresing the product $E\alpha_T$ of the carrier;

- increasing the ultimate stresses of the supporting material;

- increasing the thermal conductivity of the carrier;

- reducing the temperature difference $T_d - T_i$;

- reducing the typical dimension of the pellets.

The first three solutions would entail radical changes of the physical ancd chemical nature of the substrate and cannot be implemented in the present case because the catalyst impregnation technique developed in the framework of the present activity has been specifically designed for alumina-based substrates. The forth solution is feasible but impractical, since it would require pre-heating of the catalytic bed. Hence, the last solution has been investigated in the context of the present work.
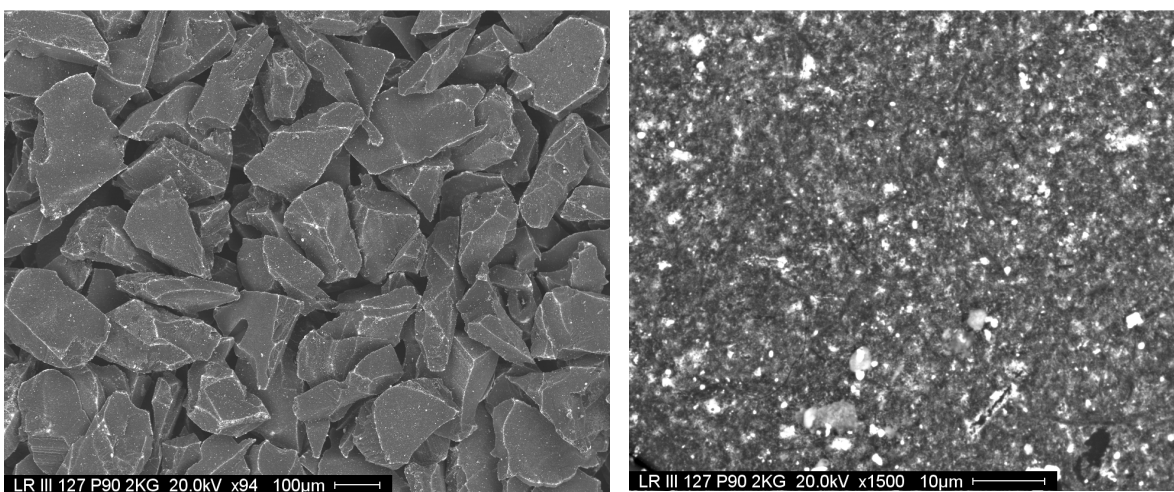

Figure 3 SEM pictures of the LR-III-127 before the reaction (left) and 1500× enlargement (right) of LR-III-127 surface after the firing test.

III. Catalysts

The core of the hydrogen peroxide monopropellant thruster is represented by the catalytic decomposition reactor. In collaboration with the Chemistry and Industrial Chemistry Department of Pisa University, ALTA S.p.A has developed a series of advanced beds based on novel techniques for catalyst implantation on ceramic supports. As a result of a preliminary screening, metallic platinum has been selected as the active metal for H_2O_2 decomposition and the development of catalyst preparation techniques has been especially focussed on platinum deposition on γ-alumina spheres with a diameter of 0.6 mm.

Previous tests results in a thruster prototype[1] have revealed the occurrence of fracture of the γ-alumina support as a consequence of thermal shocking. The catalyst preparation techniques have therefore been adapted to different alumina-based substrates, leading to the development of a Pt/α–Al_2O_3 named LR-III-127. The substrate consists of 100 μm alpha-alumina granules with 2 m^2/g of surface area, supplied by CERAC Inc. Figure 3 illustrates a SEM picture of LR-III-127 sample before the decomposition reaction and a 1500× superficial enlargement after the firing test in the rocket engine prototype. SEM analysis showed the regular granulometry of the carrier and the homogeneous deposition of platinum. No changes of the platinum load have been detected by EDX spectra on the spent catalyst. This finding demonstrated the effectiveness of the preparation technique in effecting the deposition of

platinum even on a carrier with relatively low value of the surface area. Table 3 summarizes the main characteristics of the LR-III-127 catalyst used in the present experimental campaign.

Table 3. Properties of the LR-III-127 catalyst

Identification code	Catalyst	Support	Nominal metal load (wt %)	SEM metal load (At%)
LR-III-127	$Pt/\alpha–Al_2O_3$	*100 µm CERAC alumina*	*2*	*0.8*

The catalyst load in percent atomic content (At%) is shown in the last column of Table 3. It refers to the average SEM reading over the optical framing window (200 × 180 µm) and down to the typical penetration depth of the electron beam below the catalyst surface (about 200 atomic layers).

IV. Test Apparatus

A. Thruster Prototype

In order to characterize the propulsive performance of LR-III-127 catalyst a reconfigurable monopropellant thruster prototype has been used. Several endurance tests (Torre et al.[3]) have already been performed with the same device on different advanced catalytic beds. For a total firing time of about 2 hours the prototype has proved to correctly operate both in continuous and pulsed mode. Figure 4 shows a picture of the thruster prototype used in the experiments for LR-III-127 catalyst.

The thruster has been designed to operate with 5 g/s of 90% H_2O_2 at different chamber pressures developing a nominal thrust of 6 N. The catalytic bed of the monopropellant thruster prototype has been realized by means of a modular cartridge for rapid reconfiguration and simplified filling with the catalyst pellets. The cartridge consists in a 36 mm I.D. AISI 316L stainless steel casing, long enough to accommodate a 100 mm long catalyst bed between the upstream spring-loaded injection plate and the downstream distribution plate.

Two AISI 316L stainless steel screens (230 mesh size and 0.1 mm wire diameter) are interposed between the plates and the catalyst for retaining granules with dimensions higher or equal to 62 μm. Cylindrical inserts with different lengths (*L* = 30, 60, 90 mm) and inner diameter (*D* = 18 and 25 mm) can be inserted inside the cartridge before filling with the 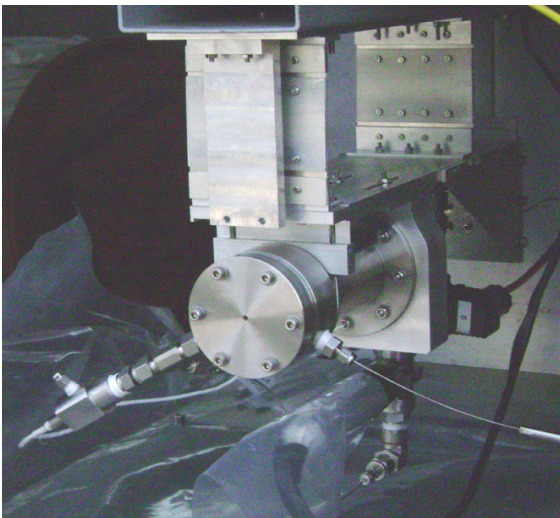catalyst pellets, allowing for easy and independent control of both the dwell time τ and the bed load *G*. Tight tolerances have been used in order to prevent HP from channeling along the clearance between the inserts and the casing. In accordance with the indications of the technical literature, the injection and distribution plates have a 50% open area ratio, realized by means of two different series of holes. The inner part of both plates has a series of 8 small holes (1 mm I.D.) for better distributing the flows of HP and decomposition products when using the highest bed load configuration, while the outer part has a series of 210 holes (1.5 mm I.D.) A central M3 threaded hole is used for connection to the extracting tool. Once assembled, the cartridge is inserted inside the AISI 316L external housing and directly retained by the HP connecting flange, which seals on two MICATHERM S15 face gaskets. The chamber pressure can easily be adjusted by replacing the separate convergent-divergent nozzle, flanged on the external housing and sealed by a MICATHERM S15 face gasket. The monopropellant thruster prototype has

Figure 4. Picture of the thruster before a firing test

been designed in order to be easily interfaced with the thrust balance of Alta's Green Propellant Rocket Tests Facility (GPRTF). More details about the prototype can be found in Torre et al.[3]
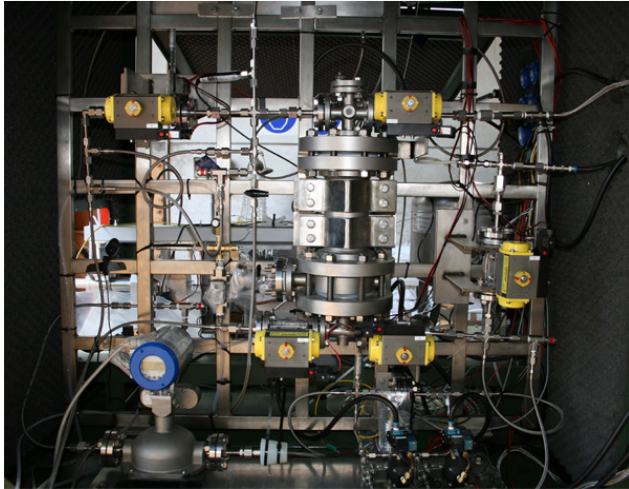
B. Test Facility

Figure 5. ALTA's GPRTF: feeding system.

The experimental campaign has been carried out in Alta's Green Propellant Rocket Test Facility (GPRTF, Figure 5), an easily reconfigurable and expandable experimental apparatus especially designed for performance characterization of small monopropellant (H_2O_2) and bipropellant (H_2O_2-hydrocarbon) rocket engine prototypes and catalytic reactors operating at thrust levels in the 1-10 N and 25-100 N ranges. The facility mainly comprises the propellant feed systems and the thrust balance. All of the hydrogen peroxide lines and main tank are made off AISI 316 stainless steel internally coated with Teflon. Hydrogen peroxide is stored in a 2.5 liters tank and is pressurized by means of Nitrogen. Its physical conditions are continuously monitored by means of a J-type thermocouple and a gauge pressure transducer. If the peroxide starts to decompose, the tank can be vented to the atmosphere by means of a remotely controlled valve or, in the absence of the operator, by the combination of a first

a relief valve and a burst disc calibrated for opening at suitably spaced pressure values. The hydrogen peroxide mass flow rate is controlled by means of interchangeable cavitating venturi and it is monitored by a Coriolis flowmeter. The operation of the venturi is continuously monitored by a differential and a downstream pressure transducer.

The thruster is mounted on a one degree-of-freedom dynamometric force balance. A number of transducers have been installed for evaluating the performance of the thruster prototype and the catalytic reactor. In particular, the conditions of the thrust chamber downstream of the catalytic bed are monitored by means of a K-type thermocouple placed on the chamber axis and by an absolute pressure transducer, which has been mounted recessed for protection from the high temperatures developing during chamber operation. A subminiature compression load cell, mounted on the balance cradle, measures the engine thrust. The performance of the catalytic bed is monitored by measuring the absolute pressure after the injector and the differential pressure between the supply line to the injector and the thrust chamber. More details about the GPRTF can be found in Pasini et al.[5]

V.   Experimental Results and Discussion

The LR-III-127 catalyst has been tested with a nominal bed load of 19.65 kg/s m[2] and a chamber pressure of 10 bar. For the experiments a catalyst volume of 15 cc of catalytic granules has been contained in a cylindrical chamber 60 mm long and with an inner diameter of 18 mm.

A. Catalytic Bed Main Parameters

The characteristic velocity efficiency (η_{c*}) and the temperature efficiency ($\eta_{\Delta T}$) have been used for quantitatively assessing the effectiveness of catalytic bed in decomposing HP for thrust generation. They are respectively defined as:

$$\eta_{c*} = \frac{c^*_{exp}}{c^*_{theo}} = \frac{\dfrac{p_c^{exp} A_t}{\dot{m}_{exp}}}{\sqrt{\dfrac{RT_{ad}}{\gamma}}\left(\dfrac{\gamma+1}{2}\right)^{\frac{\gamma+1}{2(\gamma-1)}}} \tag{5}$$

$$\eta_{\Delta T} = \frac{T_{exp} - T_{amb}}{T_{ad} - T_{amb}} \tag{6}$$

The $c*$ efficiency expresses the ratio between the measured characteristic velocity and the theoretical one, computed using the 1D ideal rocket equations and the nominal adiabatic decomposition temperature (T_{ad}) of the propellant. Its value, lower than one, takes into account both the chemical performance of the catalyst, which can reduce the decomposition temperature below its nominal value, and the non-idealities of the gas transit through the thrust chamber and the expansion nozzle. On the other hand, the temperature efficiency mainly accounts for the catalyst performance, expressing how close the measured chamber temperature is to the adiabatic temperature corresponding to complete decomposition of the propellant.

Another important operational parameter is the pressure drop across the catalytic bed, whose magnitude adversely affects the weight of the propellant storage system. However, an excessive reduction of the bed losses reduces the fluid dynamic damping in the bed, exposing the chamber to the risk of development of self-sustained flow oscillations. Bed losses also represent the primary source of catalyst pressurization during the engine start-up. Their excessive reduction retards the pressurization of the catalyst, decreasing the propellant decomposition rate and increasing the length of the start-up transient. Finally, the variation of the catalyst pressure drop gives indications about the ageing of the bed an in particular of the occurrence of thermal fracture of the catalyst pellets.

The experimental campaign on LR-III-127 catalyst has been conducted using a hydrogen peroxide solution in concentration of 90% ±0.8%.

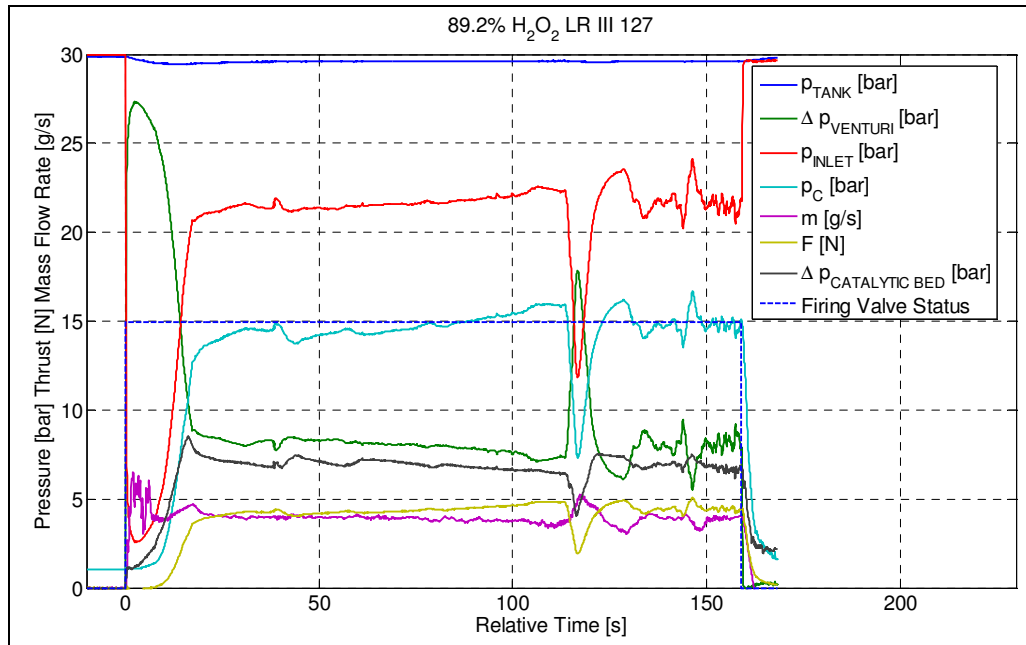**Figure 6. Experimental results on LR-III-127 catalyst tested with an actual H_2O_2 concentration of 89.2% and $G = 15.72$ kg/m²s ($\tau = 5.30$ s).**

B. LR-III-127 firing test

The firing has been carried out at constant upstream pressure of the propellant and comprised an initial transient phase (lasting about 12 s) for complete start-up of the catalytic reactor, followed by a longer steady-state operation (lasting about 150 s) up to the complete depletion of the H_2O_2 tank. Nominal working conditions have not been

achieved because the high pressure drop across the catalytic bed (about 7 bar) has not allowed for the cavitating venturi to work correctly. As a result, at steady-state conditions the mass flow rate was 4.00 g/s rather than 4.91 g/s (see Table 4) and also the bed load G was lower than expected. This in turn increased the dwell time of hydrogen peroxide on the catalyst. The higher value of pressure drop (about one order of magnitude greater than in previous experiments[5]) is mainly due to the significant decrease of the size of the catalyst granules with respect to the alumina substrates formerly used for other catalysts[3,4,5]. Other contributing factors are the reduction of the chamber pressure with respect to the nominal value and the high value of the decomposition temperature, which increase the flow velocity and consequently the pressure losses at constant propellant mass flow rate.

The time-histories of the chamber temperature, of the decomposition temperature efficiency and of the C-Star efficiency during the firing test are reported in Figure 7 and Figure 8, respectively. A rather high value of the decomposition temperature (970 K) has been attained, confirming the catalytic effectiveness of the bed. The temperature and characteristic velocity efficiencies also resulted to be remarkable (see Figure 8), reaching values of 95% and 96% respectively.

The experimental measurements turned out to be less regular than in previous experiments because the lack of the cavitating venturi on the propellant supply line to the thruster made the mass flow rate sensitive to the occasional fluctuations of the chamber pressure. The drastic decrease of chamber pressure at a relative time of 120 s is most probably due to channelling, rather than to the decrease of the mass flow rate, as confirmed by the appearance of partially decomposed hydrogen peroxide in the exhaust plume. It is possible that a leakage of liquid H_2O_2 occurred either on the insert external wall or through the catalyst in consequence of the high pressure drop across the catalytic bed. However, contrary to the results of previous experiments with larger pellet size, the progressive occlusion of the catalytic bed due to the thermal rupture of the ceramic spheres did not occurr in present experiments. As shown in Figure 6, the pressure drop across the catalytic bed remained nearly constant during the 150 s firing test and no important flow instability has been detected.
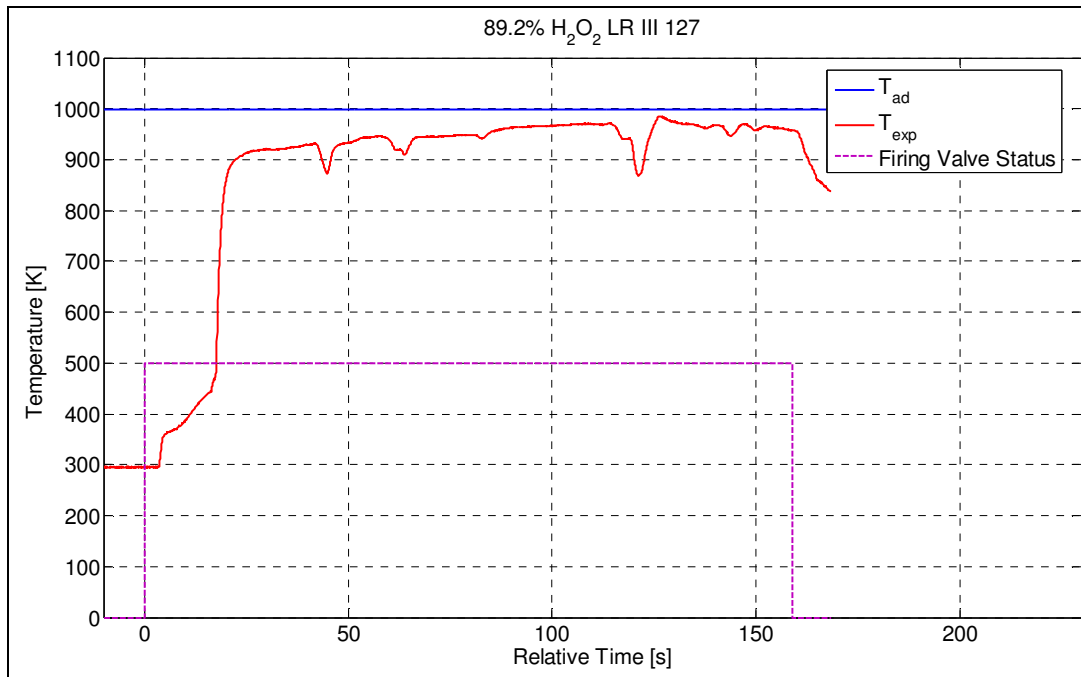

Figure 7 Chamber temperature for the LR-III-127 catalyst tested with 89.2% HP at G = 15.72 kg/s m^2 and τ = 5.30 s.

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Table 4 Steady-state performance with LR-III-127 catalyst

| Performance	LR-III -127	Ideal Adiabatic Decomposition
Bed load	15.72 kg/s m^2	-
Dwell time	5.30 s	-
Mass flow rate	4.00 g/s	4.00 g/s
Chamber pressure	14.75 bar	15.25 bar
Chamber temperature	970 K	998 K
Characteristic velocity	885 m/s	923.0 m/s
Thrust	4.5 N	4.75 N
Thrust coefficient	1.29	1.35
Specific impulse	117 s	136 s
Vacuum specific impulse	160 s	171 s
Catalytic bed pressure drop	7 bar	-
$c*$ efficiency	0.96	-
ΔT efficiency	0.95	-
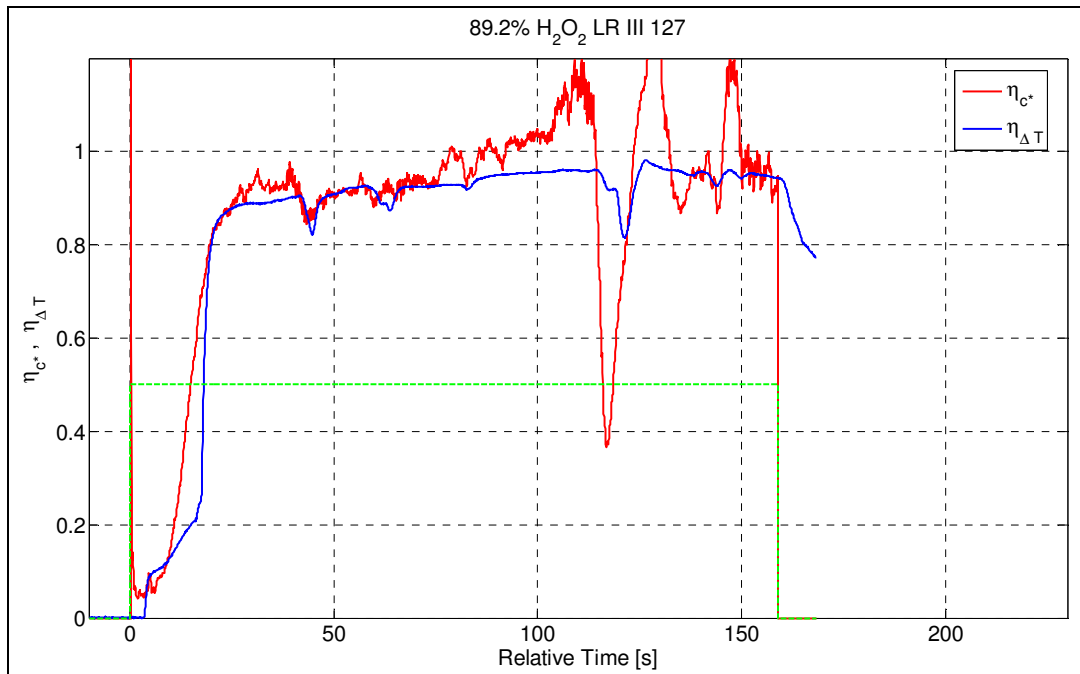
Figure 8 Temperature and $c*$ efficiencies for the LR-III-127 catalyst tested with 89.2% HP at G = 15.72 kg/s m^2 and τ = 5.30 s.

VI. Conclusions

Thermal shocking generated by the impulsive and probabbly intermittent exposure to the high decomposition temperature of hydrogen peroxide is suspected to be the main reason for the break-up of ceramic pellets in HTP catalytic beds. Two different fracture modes have been identified in previous experiments: pellet rupture in two nearly equal parts when exposed to lower concentration hydrogen peroxide solutions, and surface chipping in minute fragments (powdering) during the decoposition of HTP.

For brittle ceramic pellets typically used for catalytic beds fracture can be assumed to occur when the maximum or minimum stresses exceed the ultimate tensile strength of the material. Under this assumption, the results of the present model, developed with the aim of analyzing the thermal stresses in catalytic pellets for hydrogen peroxide decomposition for small rocket applications and of interpreting previous experimental results, confirm that pellet rupture or pulverization are likely to occur in the initial portion of the catalytic bed.

The model also provides a convincing explanation for the occurrence of two different rupture modes of the pellets when exposed to hydrogen peroxide solutions of increasing concentration. The different intensity of the decomposition heat release at the pellet surface generates different evolutions of the intensity and distribution of the unstead temperature profile in the catalyst pellets. At low hydrogen peroxide concentrations, the superficial heat release is not sufficient to generate compression stresses in the outer layer of the pellet soon after contact with the propellant in excess of the relatively high value of the ultimate compression strength of the material. The subsequent propagation of the thermal wave concentrates the tension stresses in the central portion of the pellet, where fraction is nucleated as soon as the lower ultimate tensile limit of the material is exceeded, and propagates outwards breaking the pellet in two nearly equal parts. Viceversa, at higher hydrogen peroxide concentrations, the superficial heat release is capable to rapidly generate in the outer layer of the pellet compression stresses exceeding the ultimate strength of the material, producing chipping of the pellet in small fragments (powdering).

The experimental results from a series of tests on a new Pt/Al_2O_3 catalyst (LR-III-127) for H_2O_2 decomposition confirmed the possibility of solving the pellet break-up problem by using beds with pellets of smaller size (100 μm instead of 600 μm) and higher stress resistance. Outstanding propulsive performance in terms of c* and temperature efficiencies have been attained by the LR-III-127 catalyst, at the expense of increased pressure losses through the catalytic as a consequence of the reduced size of the pellets. Progressive occlusion of the catalytic bed due to the rupture of the ceramic pellets in small fragments has been eliminated.

The experience gained in the present investigation demonstrated the usefulness of the proposed model in guiding and supporting the development of effective catalytic beds for HTP and providing useful predictive indications on their relative susceptibility to thermal cracking. The experimental investigation on the LR-III-127 with high grade hydrogen peroxide (90% by weight) widely confirmed the effectiveness of the undertaken actions to improve the thermal shock resistance of the catalytic bed.

Acknowledgments

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