

A NEW Iridium SUPPORTED CATALYST, 27% Ir/Al₂O₃-Nb₂O₅, APPLIED TO SATELLITE MICROPROPULSION

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Abstract: *A new iridium supported catalyst was prepared, using a mixed oxide of aluminium and niobium as support. After characterizations, this material was tested in Test Facilities with Simulate Altitude (BTSA/LCP/INPE) in a fixed bed 5N thruster. Results of chamber pressure, engine thrust force and temperature evolution showed that this new material presents similar behavior in comparison with the iridium/Al₂O₃ catalysts S-405 and LCP33R.*

Keywords: *iridium catalyst, aluminium-niobium oxide, satellite propulsion*

1 Introduction

Catalysis means use of materials that participate in chemical reactions without been consumed and, because of the reaction mechanism modification, these can be proceed in lower temperatures and/or in higher reaction rate. Actually, in the Combustion and Propulsion Laboratory at National Institute of Space Research (LCP/INPE), subordinated to Center of Space Technologies (CTE/INPE), the main activities of research and development in Catalysis area are: Catalysis for propulsion employment; Catalysis for industrial application, Catalysis for environment and Synthesis of new materials (essential for researches and projects development in the areas written before).

1.1 History

The satellites propulsion became feasible in 1960 decade, when the American Company Jet Propulsion Laboratory, developed the catalyst called Shell 405 (S405 nowadays). This catalyst is composed by metallic iridium supported in a special alumina surface. This material has high metal content, about 30 to 35% weight,

acts in the monopropellant hydrazine (N₂H₄) decomposition reaction allowing several drives including in the ambient temperatures (at about 20⁰C).

Since 1984, in Brazil, the LCP/INPE, working for Space Technologies Engineering division (ETE/INPE) began the acquisition of equipments and specialization of crew in catalysis for this purpose. For a long time, the major problem was to develop the special alumina preparation process. This alumina must have adequate morphological and physicochemical properties, been conformed as extruded grains in a good shape to be employed in the satellites microthrusters. Actually, the national catalyst, LCP33R (33% Ir/Al₂O₃) had been tested over long periods of operation under conditions of multiple drive becoming a strategic material that makes Brazil independent of imported catalysts.

In the roll controller motors for Satellite Lancher Vehicles, they demand a great quantities of catalyst, used only one time for few minutes. In this case, INPE developed materials with low cost, as tungsten carbide and Ir-Ru/Al₂O₃ catalysts.

A new generation of catalysts for propulsion uses is now under development. The material is constituted of iridium supported on the surface of alumina-niobia (Ir/Al₂O₃-Nb₂O₅). The preliminary propulsion tests shown that presents promising results which are shown in this work.

1.2 Characteristics of Catalysts for Propulsion Uses

The active site of the catalyst (iridium) that will be employed in the satellites propulsion purpose, must be capable to decompose hydrazine after little contact time in order of milliseconds. This reaction involves two different ways:



The mechanisms of this reaction on the metal (iridium) surface of catalyst are shown in Figure 1.

The catalytic chamber, inside the thruster, is filled with spheroid grains of Ir/Al₂O₃, carefully packed. Because of temperatures and pressures variations inside the microthruster, which are extremely high and fast, turn necessary to ensure excellent heat and mass diffusion. The mass diffusion is obtained using porous alumina grains, which is synthesized to have high porous volume and specific surface area as well as high mechanical resistance.

On the surface of grains of alumina, outside and inside its pores, high weigh concentration of iridium is deposited in order that the reaction begins in the external surface of the grains and not inside the pores (because this phenomenon can cause the grains fragmentation).

The high concentration of iridium particles, with mean diameter size of 20 to 30 Angstroms, promotes the heat diffusion and avoids the appearance of hot spots. The Figure 2 shows a scheme of this catalyst grain.

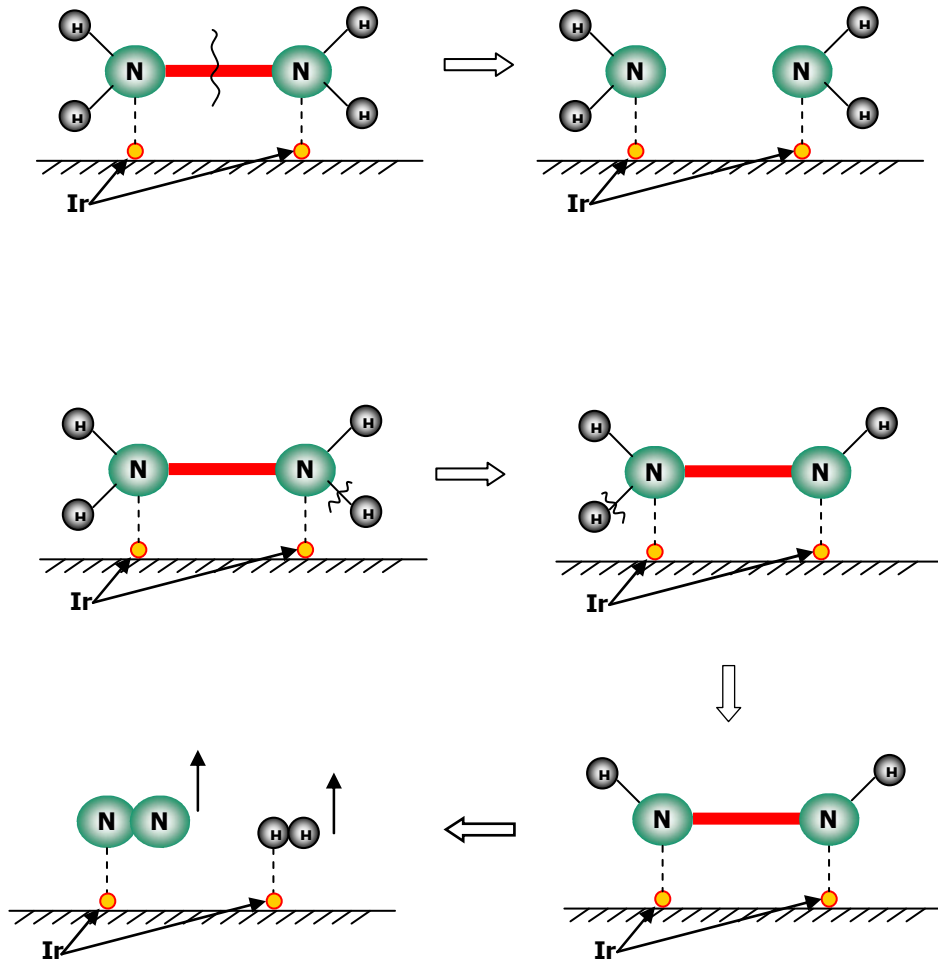


Figure 1. Hydrazine decomposition scheme on the metal iridium.

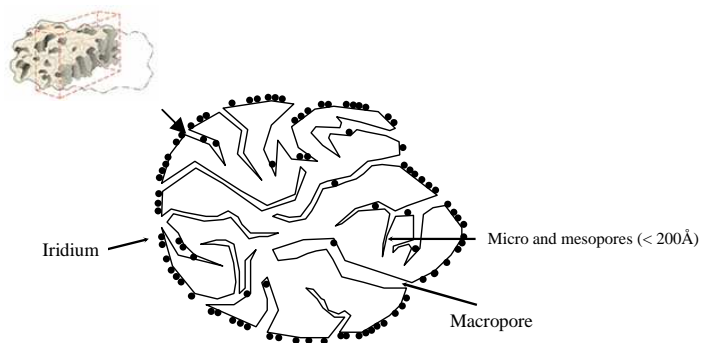


Figure 2. Iridium/alumina catalyst scheme.

In order to extend the satellite life for many years, the propulsion system has a liquid hydrazine tank, solenoids and several thrusters. Figure 3 presents a simplified propulsion system and a photo of a 5N thruster.

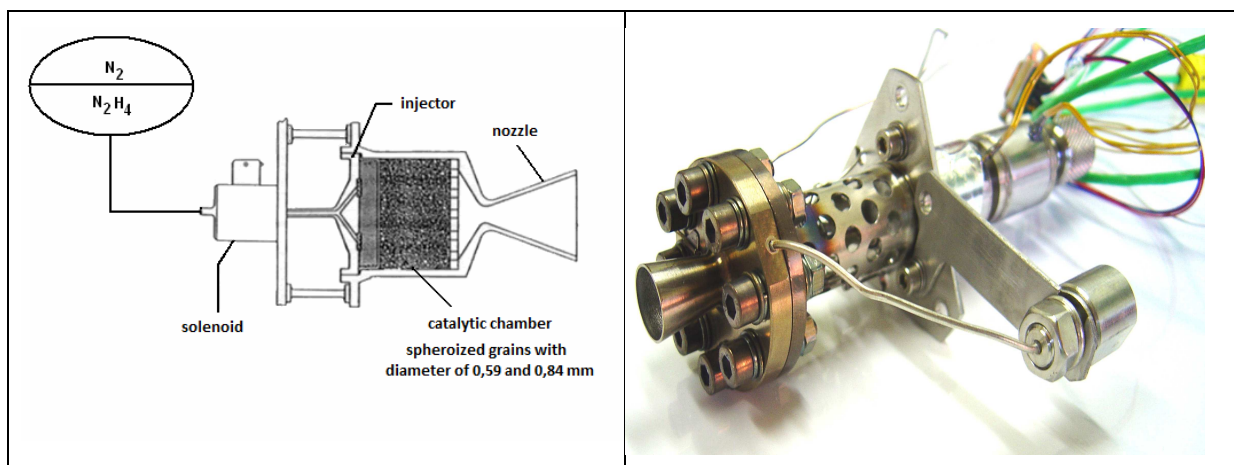


Figure 3. Satellite propulsion system scheme and a 5N thruster photo.

The objective of this work is to compare results obtained with Ir/Al₂O₃-Nb₂O₅ catalyst with S405 and LCP33R catalysts tested in the same conditions.

2 Experimental

2.1 Preparation

The preparation of the support Al₂O₃-Nb₂O₅ is schematically represented in Figure 4, and its details are described below.

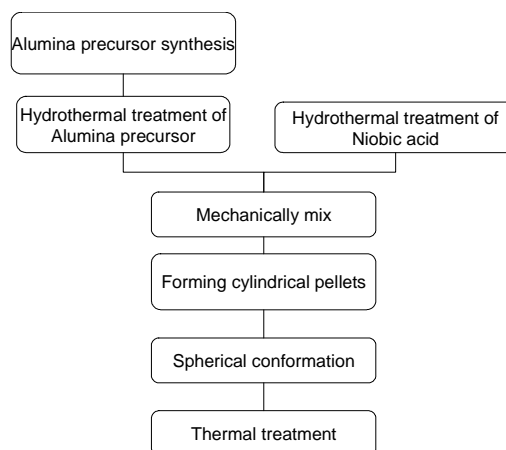


Figure 4. Flow diagram of Al₂O₃-Nb₂O₅ support preparation

Aluminium hydroxide previously synthesized was submitted at a hydrothermal treatment using the nitric acid purchased from Merck lot K38250156 in solution of 10% (v/v) mixed with niobium oxide kindly provided by CBMM lot AD/3351, also previously hydrothermal treated with the use of solution 10% (w/w) of oxalic acid (Vetec lot 045168). The resulting material was filtered, dried, redispersed using aluminium chloride hydroxide 50% solution lot 03-342B/768 provided by Queluz Química LTDA. The obtained paste was formed into cylindrical pellets, and after a drying step under 50⁰C for 12 hours, they were conformed to a spheroid form in an air mill. After a calcination at high temperature (600⁰C for 5 hours), iridium was deposited on this mixed oxide support using hexachloroiridic acid solution impregnated by a successive wetness method. Finally, a thermal

reduction treatment was made under H₂ gas ambient, resulted in the catalyst denominated 27%Ir/Al₂O₃-Nb₂O₅ (LCP27R).

2.2 Characterization

The alumina-niobia support and the LCP27R catalyst were characterized using the following techniques: X-ray diffraction (Philips model 1840/1830), scanning electronic microscopy (Jeol model JSM-5310), mercury Porosimeter (Micromeritics model Autopore III), nitrogen physisorption (Quantachrome Corporation model NOVA-1000) and hydrogen chemisorption (Quantachrome Corporation model Chembet 3000).

2.3 Propulsion Tests

After placed in a 5N thruster, as a catalyst bed, the material denominated LCP27R was tested with the hydrazine decomposition reaction, in a vacuum simulated atmosphere. This test, performed in a Test Facilities with Simulate Altitude (BTSA/LCP/INPE), produces several experimental results, including thrust force, internal pressure, and temperature profile (Figure 5).



Figure 5. Test Facilities with Simulate Altitude (BTSA) at LCP/INPE

3 Results and Discussion

Table 1 shows the sequence of tests performed with the catalyst LCP27R in a 5N thruster engine.

Table 1. Sequence of tests with catalyst LCP27R in a 5N thruster engine.

At initial temperature of 100 ⁰ C				
Test number	Hydrazine injection pressure (bar)	Pulse number	Pulse t _{on} (ms)	Pulse t _{off} (ms)
1	5,52	1	10000	-
2	5,61	1	100000	-
3	12,05	1	100000	-
4	22,03	1	100000	-
5	22,12	1	2000000	-
At initial temperature of 30 ⁰ C				
6	5,52	10	100	900
7	12,05	10	500	500
8	12,05	100	500	500
9	12,10	1	100000	-
10	12,13	1	2000000	-

Images obtained in SEM are represented in the Figure 6. These images showed that these 3 catalysts presented similarity on morphology and textural properties after tests performed in the 5N thruster system.

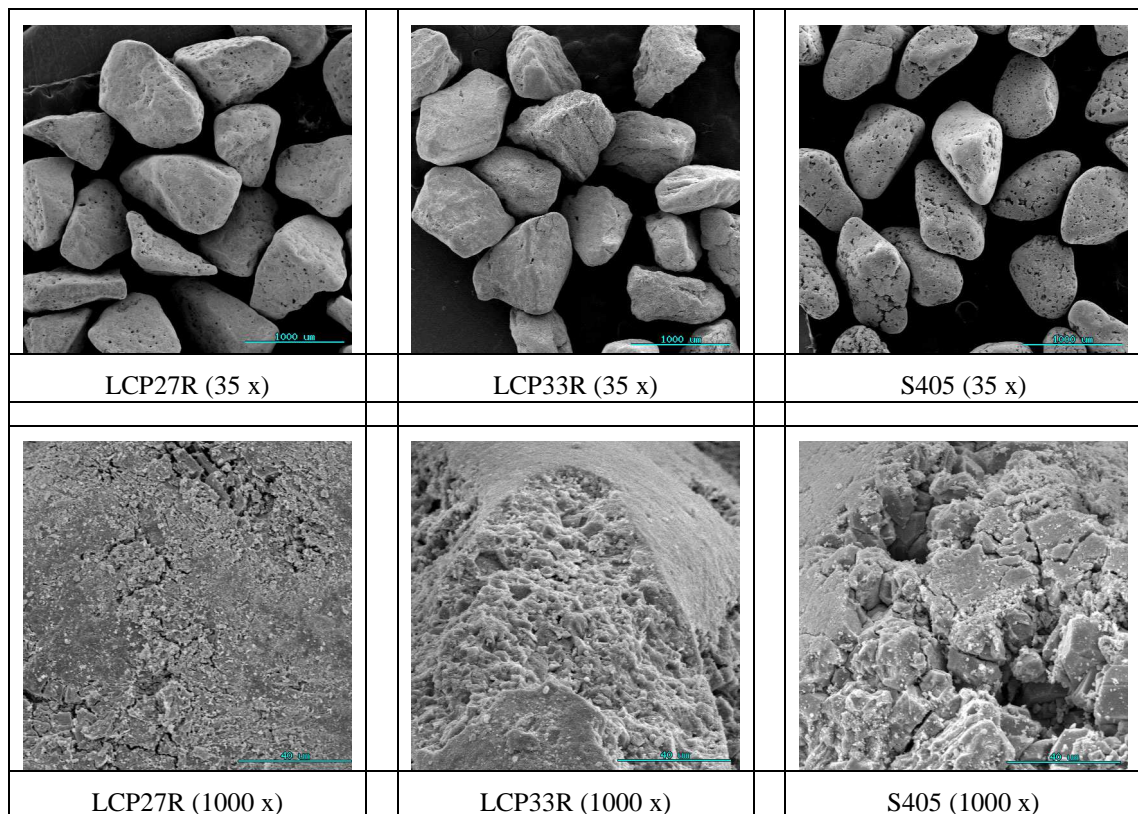


Figure 6. SEM's images of iridium catalysts supported on: alumina-niobia (LCP27R), brazilian alumina (LCP33R) and American commercial catalyst (S405), after a sequence of tests with hydrazine decomposition.

All these images show a crystal agglomerated structure with some macroporosity.

Figure 7 presents the characterization results of the three catalysts by X-ray diffraction.

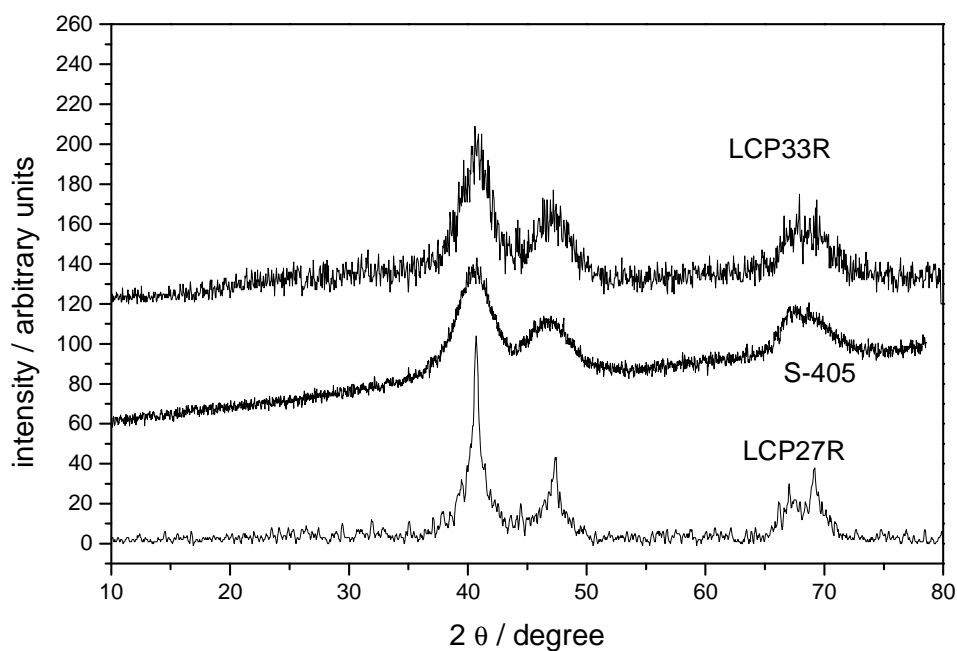


Figure 7. X-ray diffraction of 3 supported catalysts after 5N thruster test.

The X-ray diffraction shows the similarity of the three catalysts in their crystal phases. It can be observed that in the LCP27R catalyst only alumina is well crystallized.

In Table 2 are shown some properties of these catalysts as specific surface area, pore volume, average pore diameter smaller than 200 Å, and mechanical strength before the catalyst test and in Table 3, all these parameters after the catalytic tests in the 5N thruster.

Table 2: Specific surface area, pore volume, average pore diameter less than 200 Å, and mechanical strength before the 5N thruster tests.

catalysts	Specific surface area (m ² .g ⁻¹)	Pore volume (cm ³ .g ⁻¹)	Average pore diameter smaller than 200 Å (cm ³ .g ⁻¹)	mechanical strength (N)
LCP27R	94 ± 4.7	0.11	47.2	14.1 ± 2.6
LCP33R	111 ± 5.5	0.15	53.4	8.4 ± 2.8
S405	106 ± 5.3	0.10	37.7	5.6 ± 2.0

These results show that the iridium catalyst supported on alumina-niobia has a lower specific surface area when compared with another two catalysts. Both of Brazilian catalysts, LCP27R and LCP33R, have mechanical strength to compression better than the American S405.

Table 3: Specific surface area, pore volume, average pore diameter less than 200 Å, and mechanical strength after the 5N thruster test

catalysts	Specific surface area (m ² .g ⁻¹)	Pore Volume (cm ³ .g ⁻¹)	Average pore diameter smaller than 200 Å (cm ³ .g ⁻¹)	mechanical strength (N)
LCP27R	55 ± 2.7	0.10	74.9	13.0 ± 3.9
LCP33R	71 ± 3.5	0.13	75.2	9.3 ± 2.0
S405	54 ± 2.7	0.10	72.6	5.6 ± 1.7

After catalytic tests, all materials presented considerable decreased of their specific surface area but all them maintained their mechanical strength to compression. When all of these catalysts are compared, LCP27R maintained its higher mechanical strength.

Table 4 shows the evolution of catalysts active phase (Ir) during the sequence of catalytic tests . These results are obtained using hydrogen chemisorption method.

Table 4: Evolution of metallic iridium phase of the three catalysts during sequence of tests in a 5N thruster.

catalysts	Before Tests		After Tests	
	Dispersion	Mean diameter size	Dispersion	Mean diameter size
	D (%)	Dp (Å)	D (%)	Dp (Å)
LCP27R	29	31	10	90
LCP33R	42	21	18	50
S405	46	20	23	39

The dispersion corresponds to the percentage of total atoms of iridium situated on the surface of the support. It was calculated by H₂ chemisorption, considering the stoichiometry of chemical adsorption H:Ir (1:1). The mean diameter size of the metallic particles was calculated, considering that they present a semi-sphere form, employing the empirical equation

$$\overline{dp}(nm) = \frac{90}{D(\%)} \quad (3)$$

Table 4 shows that the LCP27R catalyst presents the lowest dispersion value and, consequently, the highest mean diameter size of the Ir particles. These results can be attributed to the fact that the iridium particles are preferentially deposited on the alumina, while their deposition on niobium oxide is much lower. This conclusion is confirmed by Electron Dispersion Spectrometry (EDS), which results are presented in the Figure 8.

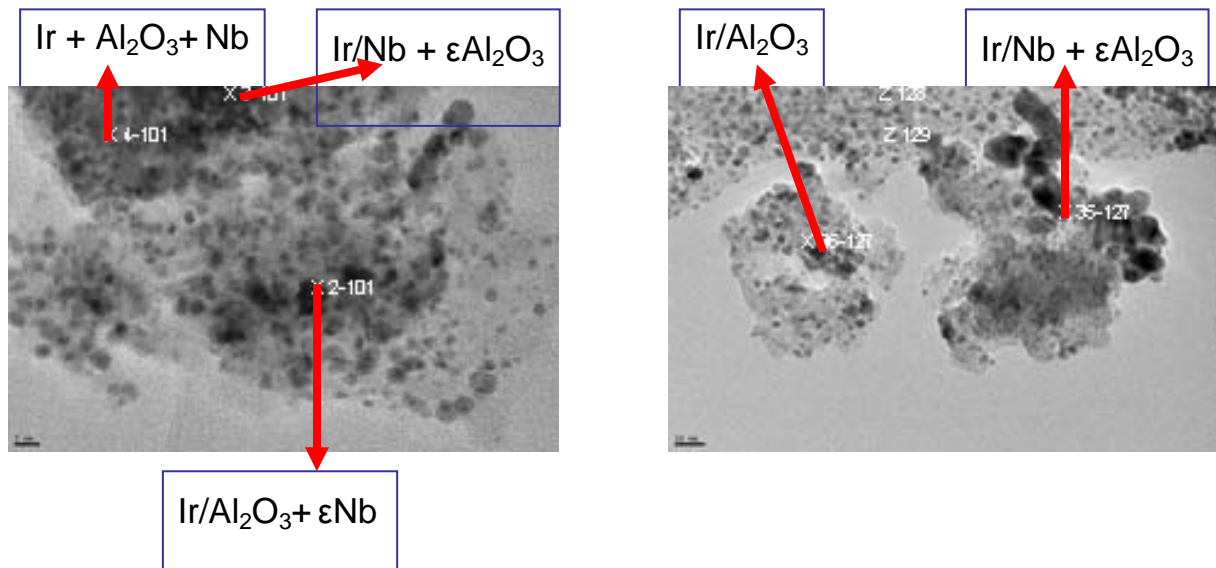


Figure 8. Distribution of iridium particles on alumina and niobia support of LCP27R catalyst, determined by EDS technique.

The high concentration of iridium particles on the alumina of the support explains the higher growth of their mean diameter size, by a sintering process, after tests.

Figures 9 to 11 show the results of force, internal pressure and the temperature evolution. These results permit conclude that the 3 catalysts presented similar results.

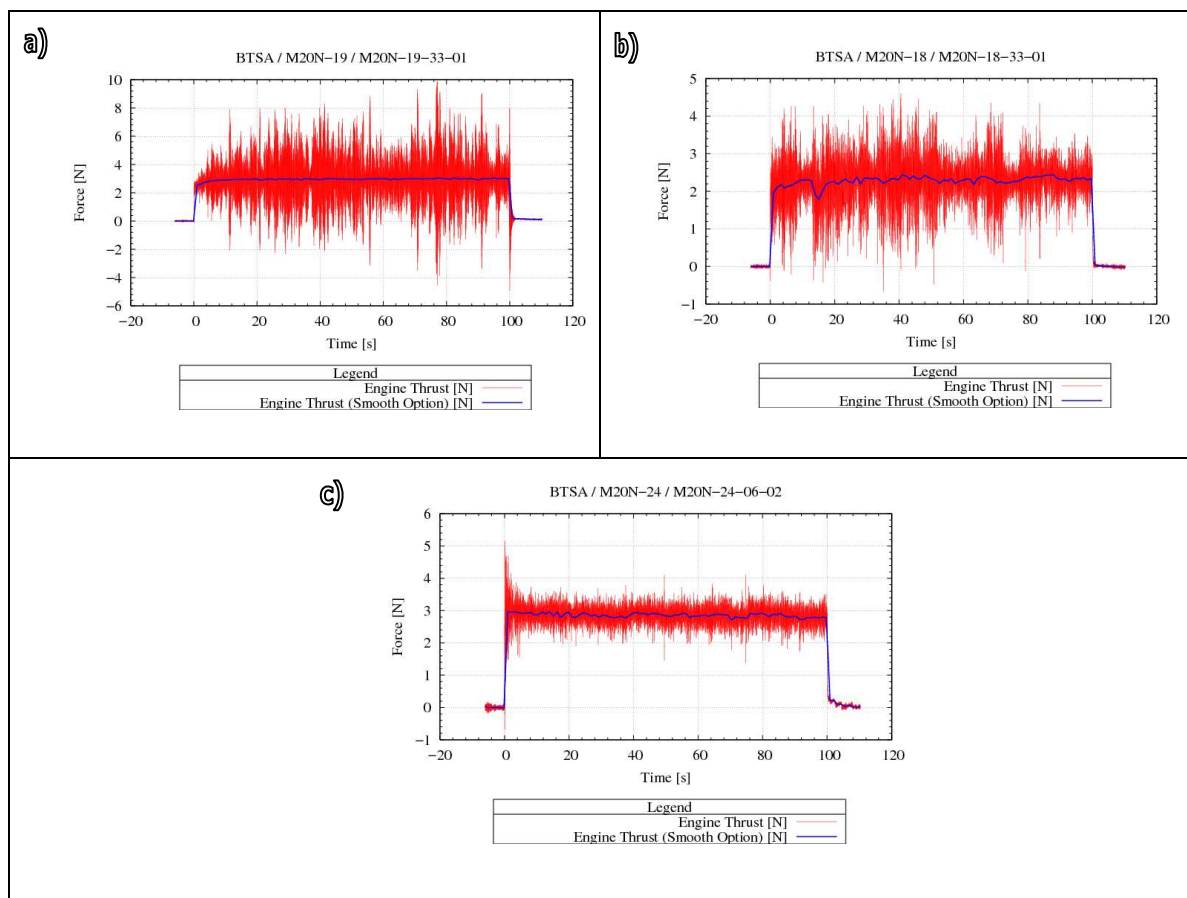


Figure 9. Catalytic Chamber Engine Thruster Force using tank pressure of 12 bar, 100s of continuous action time for: a) S405, b) LCP33R and c) LCP27R

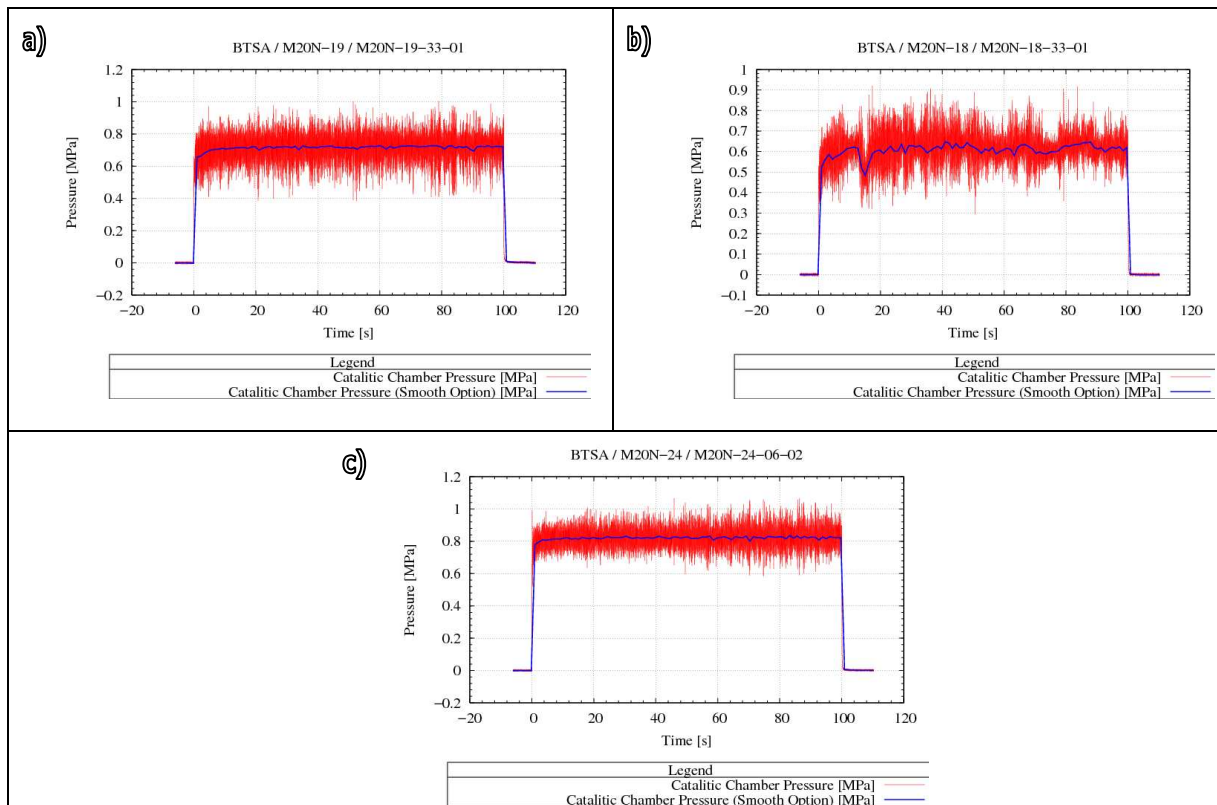


Figure 10. Catalytic Chamber Pressure for a 5N thruster using 12 bar of tank pressure, 100s of continuous action time for: a) S-405, b) LCP33R and c) LCP27R

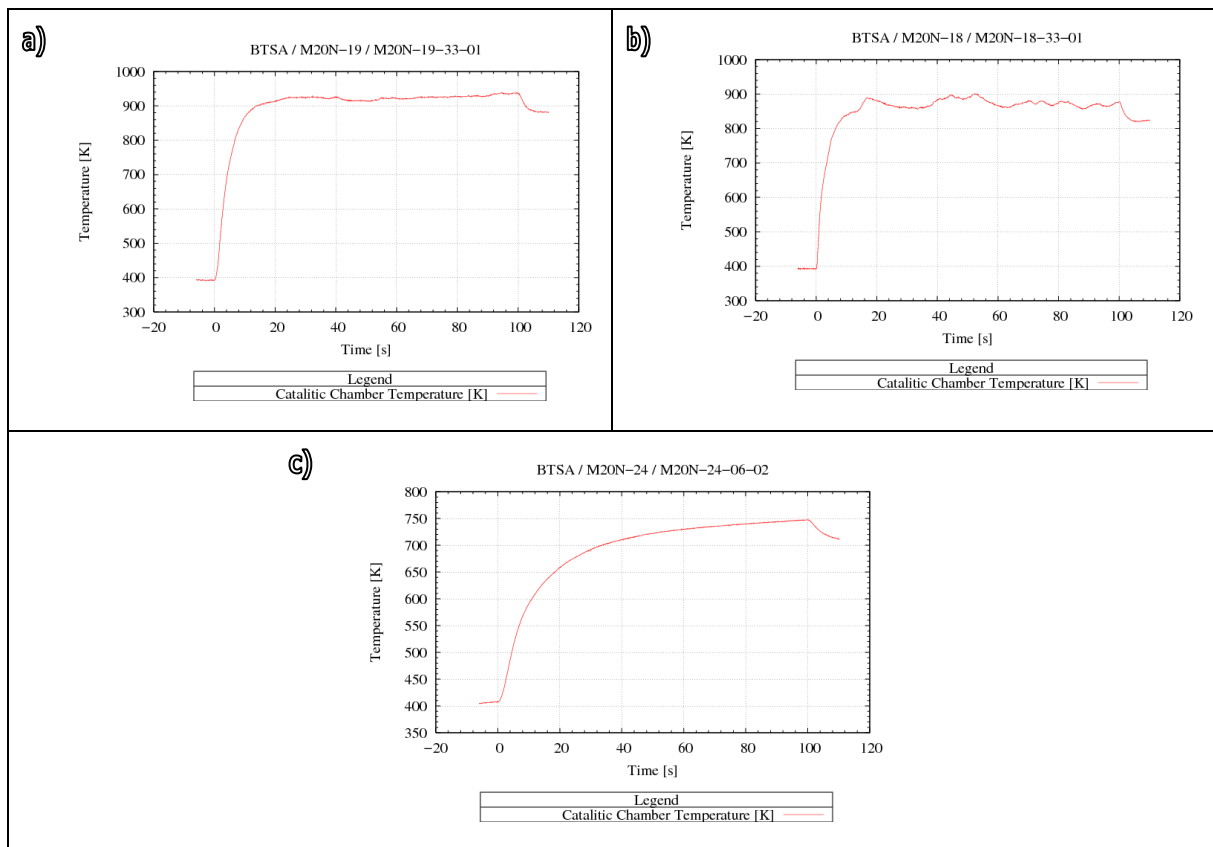


Figure 11. Evolution of the catalytic chamber temperature in a 5N thruster operating with tank pressure 12 bar, 100s of continuous action time for: a) S405, b) LCP33R and c) LCP27R

4 Conclusions

- 1 – The support obtained by mechanically mixing method of alumina and niobia conducted to a material where only alumina presents crystallinity by X-ray diffraction;
- 2 – Metallic iridium particles have been deposited preferentially on the alumina phase of support;
- 3 – Despite of a lower metallic dispersion, the LCP27R showed similar behaviour in comparison with the two other catalysts, LCP33R and S405;
- 4 – Nevertheless its lower metallic dispersion, the LCP27R good behaviour can be attributed to a better dissipation of heat flow, caused by niobium oxide, which decreases the existence of hot points in the internal structure of this catalyst and reduces its loss of mass, limited to only 5,4% during the sequence of the tests.

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