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Hydrazine decomposition over niobium oxynitride with macropores generation

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Abstract

The aim of this work is to employ niobium oxynitride with macropores generation in the hydrazine decomposition reaction as substitute of iridium supported catalysts used for space communication satellites, which are equipped with microthrusters that control their orbit and attitude. The performance of niobium oxynitride was compared to tungsten oxynitride and Shell 405 catalyst. ©2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

The use of liquid hydrazine for propulsion was studied initially by Jet Propulsion Laboratory (JPL) [1]. Initial results showed that the thermal decomposition of hydrazine is slow, presenting too elevated induction times for practical applications in propulsion. The first catalyst developed by JPL was Fe–Co–Ni/Al_2O_3 which showed a good performance in hydrazine decomposition. A few years later, a private company, Shell metals, developed a new catalyst named Shell 405^{TM} (30% Ir/Al_2O_3) that activated the hydrazine decomposition at only 293 K. The disadvantage of this catalyst is its high cost due to the facts that it is based in a special type of alumina and that iridium is a rare and very expensive element.

It is found in the literature that (oxy)nitrides and (oxy)carbides of Ti, V, Nb, Mo and W are able to be a substitute of noble metals like Ir, Pt and Pd [2–11]. The (oxy)nitrides and (oxy)carbides of molybdenum and tungsten were tested as substitutes of iridium for the catalysts used in hydrazine decomposition for space communication purposes by Rodrigues et al. [12–15]. The performance of tungsten carbide and Ir supported catalyst were compared versus time, in a thrust rocket engine of 2 N. For a same consumption of hydrazine for both catalysts, the tungsten carbide yielded a thrust higher than that of the Ir/Al_2O_3. Furthermore, for the same continuous feed rate (0.9 g s^{-1} of hydrazine at 2×10^7 Pa), specific impulse was also higher over tungsten carbide. Another important result was that after 300 pulses of 200 ms followed by a continuous feed of hydrazine for 200 s, a lower amount of fine parti-

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cles formed from extrudates was observed in the case of the carbide (0.9 wt.%) compared to that produced from the iridium supported catalyst (1.9 wt.%).

In the present work, the niobium oxynitride extrudates were prepared with macropores generation from niobium oxide in a extruded shape with controlled volume and pore distribution [15–19]. These characteristics make this oxide attractive as niobium carbides and nitrides precursor, which potentially can be employed in catalytic systems involving fast and exothermic reactions like hydrazine decomposition. The oxynitride was prepared by reaction of the molded niobium pentoxide with flowing ammonia, at atmospheric pressure.

The resulting material was characterized by X-ray powder diffraction (XRD), physisorption of nitrogen at 77.3 K, mercury porosimetry and the elemental analysis of O, N and Nb was performed after nitridation.

The tests were performed in (i) *laboratory scale* at 333 K and atmospheric pressure under flowing hydrazine in helium; (ii) *thrust rocket engine of* 2 N containing the catalytic bed, placed in a vacuum chamber.

The performance of this catalyst was compared to those of tungsten oxynitride and Shell 405 catalyst.

2. Experimental

Nb_2O_5–HY-340 was kindly supplied by CBMM (Companhia Brasileira de Metalurgia e Mineração, Brazil) as a precursor of niobium oxynitrides.

The optimization of niobium oxides molding process was developed to produce an extruded shape presenting controlled volume and pore distribution with good mechanical strength [15–19], used as a precursor of niobium oxynitrides.

The next step was to prepare an oxynitride from the extrudates following the method of Boudart and Volpe [4–5]. Reaction with ammonia at atmospheric pressure was carried out in a tubular quartz reactor. The heating rate was 3.0 K min^{-1} and the final temperature was 923 K. The nitridation was maintained for 6 h at the final temperature.

The product was cooled to room temperature under flowing helium following passivation with a mixture 1 wt.% O_2 in helium before exposure to air.

A gas chromatograph (GC) using a thermal conductivity detector (TCD) and an automatic injection valve was employed to analyze the gas-phase composition at the outlet of the reactor. Nitrogen and ammonia were separated on a 2 m, 1/8 in. chromossorb 102 column with helium as carrier gas.

Specific surface area (S_g) of the final material was determined by physisorption of nitrogen at 77.3 K and calculated using the BET method. The pore size distribution was obtained from Quantachrome-Autoscan 33 mercury porosimeter.

A Philips PW1830 diffractometer was used for XRD patterns using a Cu Kα radiation.

The elemental analysis in O, N and Nb was performed using a combustion method.

The hydrazine decomposition in *laboratory scale* was carried out in a tubular glass dynamic-differential reactor at 333 K and atmospheric pressure under flowing hydrazine in helium.

A GC using a TCD was also used to analyze the gas-phase composition at the outlet of the reactor. Nitrogen and hydrogen were separated on a 2 m, 1/8 in PM-5 Å molecular sieve with helium as a carrier gas.

Another test was made under vacuum, in a *thrust rocket engine of* 2 N containing the catalytic bed. The catalyst performance was evaluated varying the hydrazine injection pressure and the injection time, and monitoring the thrust chamber stagnation pressure and chamber wall external side temperature. The initial bed temperature was 353 K and the tests were performed in pulsed regime from 20 to 200 ms and the frequency was 1 Hz for all tests.

In both types of tests, the performance of niobium oxynitride was compared with that presented by a tungsten oxynitride prepared by Rodrigues [15] with the following characteristics:

- specific surface area: 80 $m^2 g^{-1}$;
- total pore volume: 0.03 $cm^3 g^{-1}$;
- pore volume (dp≥1000 Å): 0.003 $cm^3 g^{-1}$;
- extruded dimensions: 2.0 mm length and 1.0 mm diameter;
- crystal structure: f.c.c. phase.

Another material used for comparison was the Shell 405 catalyst [20], whose principal characteristics were:

- 29.7% Ir/γ-Al_2O_3;
- specific surface area: 115 $m^2 g^{-1}$;
- total pore volume: 0.18 $cm^3 g^{-1}$;
- pore volume (dp≥1000 Å): 0.06 $cm^3 g^{-1}$;
- metallic surface area: 33 $m^2 g^{-1}$;
- sphere dimensions: 0.6–0.8 mm diameter.

Table 1
Hydrazine decomposition rates at 333 K

Sample	r ($\mathrm{mol_{N_2}\,s^{-1}\,m^{-2}}$)
$\mathrm{NbN_xO_y}$ (without reduction)	6.4×10^{-8}
$\mathrm{NbN_xO_y}$ (with reduction)	5.4×10^{-8}
$\mathrm{WN_xO_y}$ (with reduction)	2.8×10^{-7}

3. Results and discussion

3.1. Niobium oxynitride characterization

Oxynitride was synthesized by reaction of the molded niobium pentoxide under flowing ammonia, at atmospheric pressure. After nitridation, the sample total pore volume was about $0.43\,\mathrm{cm^3\,g^{-1}}$, the pore volume (dp$\geq$1000 Å)$=0.32\,\mathrm{cm^3\,g^{-1}}$ and its specific surface area was about $41\,\mathrm{m^2\,g^{-1}}$. Its crystalline structure was f.c.c. phase and the final extruded dimensions were 1.0–2.0 mm length and 0.5–1.0 mm diameter with good mechanical strength. These characteristics were considered enough for the hydrazine decomposition in a thrust rocket engine of 2 N. The elemental analysis results showed that the formula of this material was $\mathrm{NbN_{0.84}O_{0.76}}$.

3.2. Reactivity of niobium oxynitride in laboratory scale

The main objective of the niobium oxynitride preparation was to verify the reactivity of this material in hydrazine decomposition. Before tests in a thrust rocket engine, the catalyst was tested in laboratory scale.

It is known [21] that the hydrazine can be decomposed by two different routes:

$$\mathrm{N_2H_4 \rightarrow N_2 + 2H_2} \tag{1}$$

$$\mathrm{3N_2H_4 \rightarrow 4NH_3 + N_2} \tag{2}$$

The catalyst selectivity depends mainly on the metal on which the hydrazine will be adsorbed and on the reaction conditions, such as the temperature and the hydrazine partial pressure.

In this study, the preliminary evaluation of the niobium oxynitride activity, employing a laboratory scale, was carried out in low conversion rates (<5%) and the activity of the catalyst was compared with that of a tungsten oxynitride.

During the reaction, the $\mathrm{N_2H_4}$ not decomposed and the $\mathrm{NH_3}$ produced are retained in two traps placed between the reactor and the chromatograph. In these

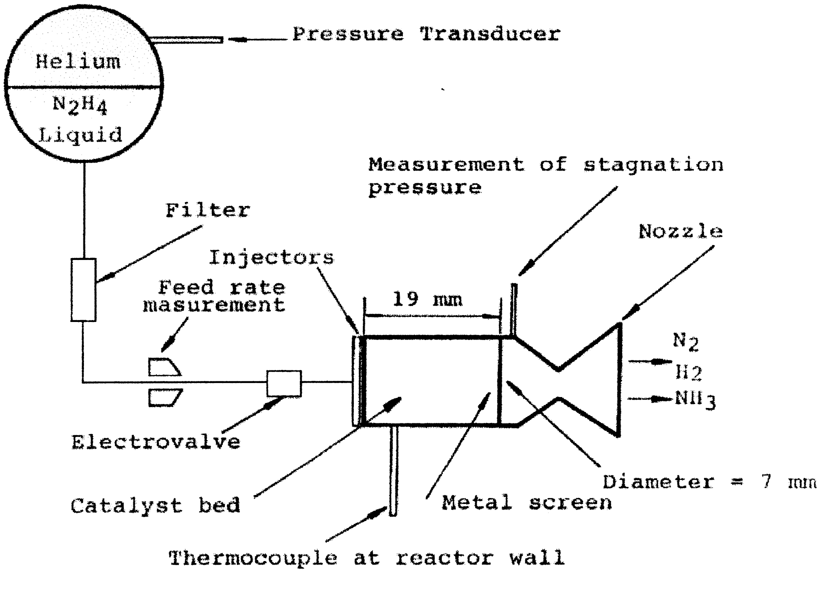

Fig. 1. Schematic diagram of the experimental system in the vacuum chamber.

conditions, only N_2 was detected, showing that the reaction is performed by route (2).

The reaction rate (r), was given by the equation:

$$r = 4.1 \times 10^{-7} P_{N_2} \frac{D_t}{m_{cat} S_g} \qquad (3)$$

where r is the reaction rate ($mol_{N_2}\,s^{-1}\,m^{-2}$), $4.1{\times}10^{-7}$=K ($mol\,kPa^{-1}\,cm^{-3}$), P_{N_2} = N_2 partial pressure (kPa), D_t the total flow rate of N_2H_4 ($cm^3\,s^{-1}$) m_{cat} the mass of the catalyst (g), and S_g is the specific surface area ($m^2\,g^{-1}$).

The niobium oxynitride synthesized was tested under flow of N_2H_4/He (55 $cm^3\,min^{-1}$) at a fixed temperature of 333 K and the hydrazine partial pressure was 0.9 kPa. The catalytic tests were performed in two phases: without reduction and with a previous treatment under flowing hydrogen at 673 K for 1 h. This reduction had the aim to make sure that the catalytic surface would be clean without passivation oxygen and chemisorbed products. The niobium oxynitride activity was lower than tungsten oxynitride (Table 1). Such result, obtained in the absence of diffusive effects, allows to suppose that the specific activity of the niobium oxynitride is lower than that of the tungsten oxynitride. Moreover, the treatment of reduction appears to be excessive, due to the decrease of the specific activity, originated by this treatment.

3.3. Reactivity of niobium oxynitride in a thrust rocket engine of 2 N

A thrust rocket engine, designed for the testing of supported iridium catalysts was used. This engine was located in a chamber evacuated down to 10^{-3} Torr (Fig. 1).

Figs. 2–4 show the typical behavior of the catalysts during a series of firings. The preliminary results of niobium oxynitride without previous reduction, in comparison with tungsten oxynitride and Shell 405™ are presented in Table 2 and showed:

- The same initial stagnation chamber pressure.
- Lower final external chamber temperature during a series of firings.

These results also seem to indicate that niobium oxynitride is less active than tungsten oxynitride and Shell 405™ [12–13]. From the comparison of these three materials in a thrust rocket engine of 2 N,

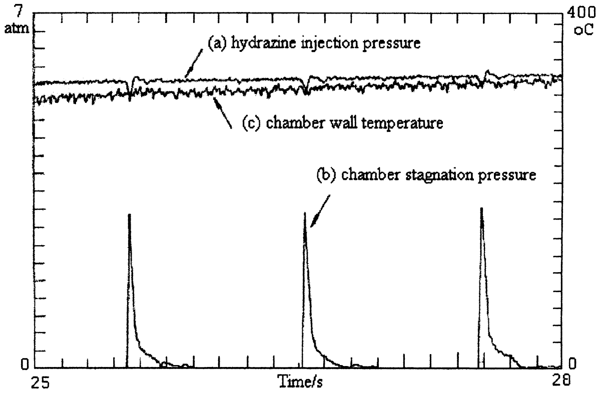

Fig. 2. Niobium oxynitride catalyst performance in pulsed regime (20 ms, 1 Hz).

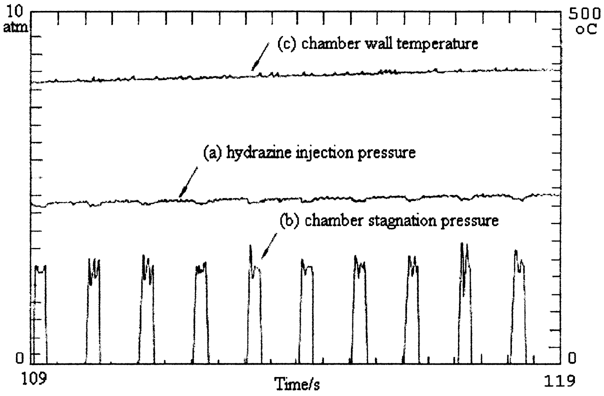

Fig. 3. Tungsten oxynitride catalyst performance in pulsed regime (200 ms, 1 Hz).

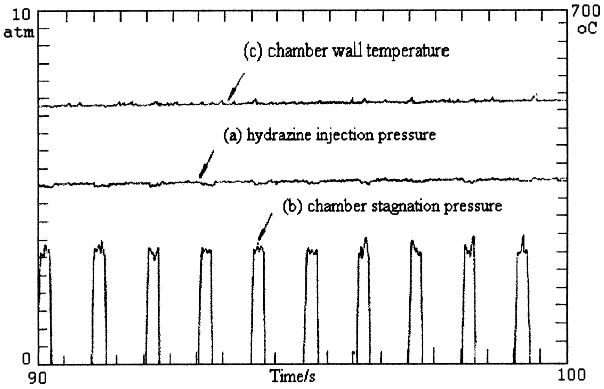

Fig. 4. Shell 405 catalyst performance in pulsed regime (200 ms, 1 Hz).

Table 2
Catalytic results of the catalysts in a thrust rocket engine of 2 N

Running	Pulse (ms) t_{on}/t_{off}	Pulse number	Hydrazine injection pressure (bar)	Chamber stagnation pressure (bar)	Chamber external final temperature (K)
NbN_xO_y test 1[a]	50/950	50	2.0	1.2	593
NbN_xO_y test 2[a]	200/800	10	5.6	2.8	473
WN_xO_y	200/800	100	5.0	3.5	633
Shell 405™	200/800	100	5.0	3.5	748

[a] Material without reduction.

another result is that the niobium oxynitride generates a less stable stagnation chamber pressure during long duration tests.

It is important to mention that the thruster was designed based in empirical rules developed for iridium catalysts configurations [22]. As described before, nitrides current granulometry and configuration are far different from those of commercial iridium catalysts and it is possible that a different thruster design or a change in nitride grains could improve the system performance, with these new materials.

4. Conclusions

Macroporous niobium oxynitride was prepared from molded niobium pentoxide and the final product presented specific surface area of 41 $m^2 g^{-1}$ and total pore volume of 0.43 $cm^3 g^{-1}$.

The activity of niobium oxynitride in hydrazine decomposition *in laboratory scale* is lower than that of tungsten oxynitride.

The performance in a *thrust rocket engine of* 2 N showed by niobium oxynitride was inferior than those of tungsten oxynitride and Shell 405™.

Modifications in thruster design and/or granulometry of niobium oxynitride can improve system performance.

Acknowledgements

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