Nitride and carbide of molybdenum and tungsten as substitutes of iridium for the catalysts used for space communication

J.A.J. Rodrigues [a,b], G.M. Cruz [b,c], G. Bugli [a], M. Boudart [d] and G. Djéga-Mariadassou [a]

[a] *Université Pierre et Marie Curie, CNRS URA 1106, Laboratoire de Réactivité de Surface, Case 178, 4, Place Jussieu, 75252 Paris Cedex 05, France*

[b] *Instituto Nacional de Pesquisas Espaciais, Rodovia Presidente Dutra, km 40, Cachoeira Paulista SP, CEP 12630-000, Brazil*

[c] *Faculdade de Engenharia Quimica de Lorena, Rodovia Itajuba-Lorena, km 74,5, Lorena SP, CEP 12600-000, Brazil*

[d] *Stanford University, Keck Science Building, Stanford, CA 94305, USA*

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Satellites are equipped with microthrusters that control their orbit and attitude. The thrust is achieved by the catalytic decomposition of hydrazine by iridium supported on alumina. As nitrides and carbides of molybdenum and tungsten behave like noble metals in many catalytic reactions, they were tried in a 2 newton hydrazine microthruster. Their performance was similar to that of the iridium catalyst, with respect to ignition delay and thrust. Their mechanical resistance appears higher than that of iridium-based catalyst. This application is the first practical one for nitrides and carbides of early transition metals as substitutes of noble metals, a possibility first reported in 1973.

Keywords: catalytic decomposition of hydrazine, MoN_xO_y catalyst, WC_xO_y catalyst

1. Introduction

In 1973, the "Platinum-like behavior of tungsten carbide in surface catalysis" was reported [1]. Since then, nitrides and carbides of other early transition metals have also been found to behave like platinum group metal catalysts [2–14]. Yet, till now, no practical application of nitride or carbide of Ti, V, Nb, Mo, W has been reported. Such an application is the subject of this report. It illustrates the frequent lag time between science and its application.

For many decades, hydrazine has been employed as a liquid propellant in small rocket engines functioning as thrusters that control the orbit and attitude of communication satellites. These microthrusters contain a solid catalyst bed that decomposes hydrazine to hot NH_3, N_2 and H_2 gases that expand through a nozzle, thus generating the required thrust after a short ignition delay.

The present work deals with new catalysts prepared as described in the literature. They are nitrides and carbides of Mo and W. These materials have a high specific surface area (100–200 m^2/g) corresponding to an ultimate crystal size of 3–5 nm. They are very refractory and do not sinter up to 1000 K, as reached in the microthrusters. Their performance in hydrazine decomposition in microthrusters will be shown to compete with that of the currently used catalyst consisting of 36% by weight of iridium supported on alumina.

2. Experimental

In the present application, finely divided new materials were prepared. In the first step of the preparations colloidal tungsten and molybdenum acids [15] were made, then peptized and finally shaped by extrusion into 1×2 mm particles large enough to be packed in a permeable bed in the microthruster [16] without being blown out by the gases produced by the decomposition of hydrazine.

The next step was to prepare nitrides and carbides from the extrudates following the method of Boudart and Volpe [4,5]. The main physico-chemical properties of tungsten carbide and molybdenum nitride are shown in table 1. The materials were then exposed carefully to oxygen in a treatment with oxygen called passivation to protect them from pyrophoric oxidation after contact with air. The final materials are designated as WC_xO_y or MoN_xO_y.

A thrust rocket engine of 2 newton, designed for the testing of supported iridium catalysts, contained the cat-

Table 1
Physico-chemical properties of catalysts

	Surface area ($m^2\,g^{-1}$)	Oxygen (wt%)	Crystal structure
WC_xO_y	50	< 5	β-W_2C
MoN_xO_y	175	< 10	γ-Mo_2N

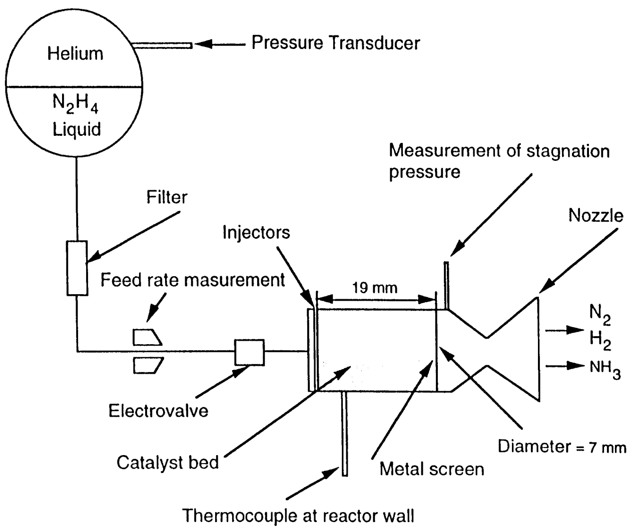

Figure 1. Schematic diagram of the experimental system in the vacuum chamber.

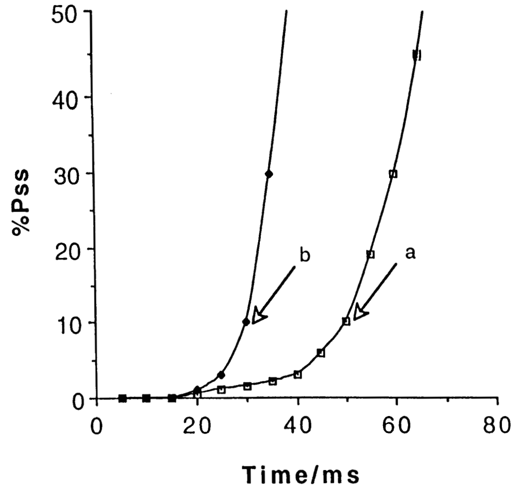

Figure 3. Comparison of ignition delays (time required for 10% of steady-state chamber pressure, (Pss)) at 2.0×10^6 Pa hydrazine injection pressure, (a) 50 ms for WC_xO_y (2 g) and (b) 30 ms for Ir/Al_2O_3 (1.5 g) in the same propulsor.

alyst bed. This engine was located with the rest of the equipment in a chamber evacuated down to 0.13 Pa (figure 1). The hydrazine injection pressure was controlled by pressurized helium to obtain the desired amount of hydrazine fed to the catalyst through an electrovalve in successive pulses or continuously (200 s). The helium pressure varied between 5×10^5 and 2×10^6 Pa.

Several parameters were monitored and/or recorded: helium pressure, flow-rate of hydrazine, stagnation pressure, thrust and temperature of the chamber. Experiments were done with or without pre-heating of the catalyst. Runs were repeated to evaluate the dispersion of data. Dispersion lower than 5% related to the mean value was found for stagnation pressure and thrust.

3. Results and discussion

Nitrides and carbides were found to be quite efficient in catalytic decomposition of hydrazine. Comparison was made with a commercial catalyst: 36 wt% iridium on γ-alumina obtained from Shell Metal Company. The run in figure 2 shows a continuous feed of hydrazine (injection pressure $= 2 \times 10^6$ Pa) for 200 s over MoN_xO_y. Two parameters related to the performances

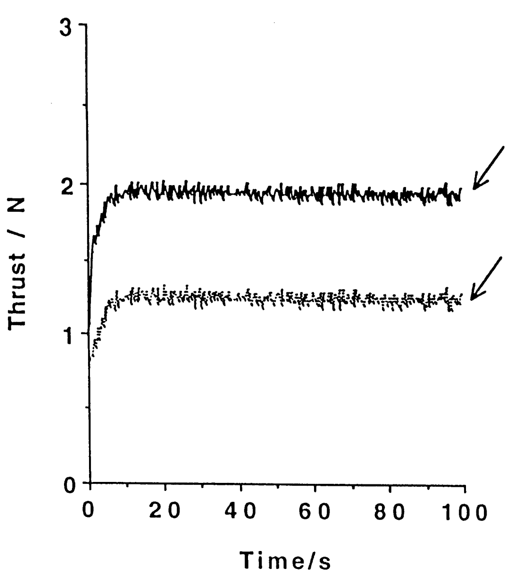

Figure 2. Comparison of catalytic decomposition of hydrazine over MoN_xO_y (1) and 36 wt% Ir/Al_2O_3 (2) in a 2 N thrust rocket engine: continuous feed.

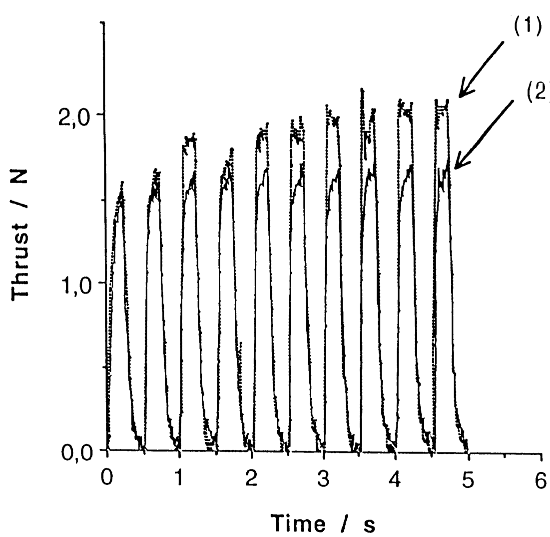

Figure 4. Comparison of catalytic decomposition of hydrazine over WC_xO_y (1) and Ir/Al_2O_3 (2), in a 2 N thrust rocket engine with a hydrazine flow-rate of 0.9 g/s at 2×10^6 Pa. Maximum temperatures at reactor wall are 1023 K for WC_xO_y and 1093 K for Ir/Al_2O_3.

Table 2
Performances of the catalysts

	Ignition delay (ms)	Steady-state temperature at reactor wall (K)	Thrust (N)	Specific impulse [a] (s)
WC_xO_y	50	953	2.1	214
Ir/Al_2O_3	30	1073	1.9	194
MoN_xO_y	90	–	1.3	133

[a] The specific impulse is a thrust force per unit weight flow and it can be expressed in "newton cubic second per meter kilogram" or more simply in seconds.

of the propulsive system can be evaluated from these data. The first one refers to the thrust produced by the system. This value is close to that obtained with the Ir supported catalyst in the same conditions. The second parameter is related to the stability of the thrust, necessary to calculate the pulse duration required for correcting the orbit of satellite. Stability can be considered as excellent as these data show a 4% dispersion of the values related to the mean pressure value observed in the chamber. This dispersion is lower than the 10% generally admitted in propulsion systems [17].

As to the ignition delay, nitrides and carbides also show good behavior. This parameter can be defined as the time interval between the opening of the electrovalve for injection of hydrazine and the time at which the pressure reaches 10% of the final stabilized pressure in the chamber. Through its own design, the opening time of the electrovalve was lower than 15 ms, whereas for nitrides and carbides, the ignition time was less than or equal to 50 ms (figure 3).

Thrusts of tungsten carbide and Ir supported catalyst are compared versus time (figure 4). For a same consumption of hydrazine for both catalysts, the two plots show that the new tungsten catalyst yields a thrust higher than that of the commonly used catalyst. Furthermore, for the same continuous feed rate (0.9 g s^{-1} of hydrazine at 2×10^7 Pa), specific impulse, defined as the ratio of thrust over propellant weight consumption rate, is also higher for WC_xO_y (table 2).

The rising of the thrust during hydrazine decomposition over WC_xO_y, as observed (figure 4), can be assumed to be due to some progressive reduction of the oxycarbide in the feed (strong reducing effect of N_2H_4) conferring a more and more metallic behaviour of the bulk catalyst.

Furthermore, the lower temperature of the reactor wall for WC_xO_y (1023 K) compared to that for Ir/Al_2O_3 (1093 K) can be assumed to be linked to the higher thermal bulk conductivity of WC_xO_y compared to that of the insulating bulk alumina support.

The higher thrust and the lower temperature of the reactor wall observed with WC_xO_y compared to those of Ir/Al_2O_3 (figure 4) are not contradictory, as both parameters depend upon the ammonia conversion (endothermic process) compared to N_2H_4 exothermic decomposition: thrust is a function of conversion degree, gas composition and resulting temperature.

Finally, preliminary results also show that after 200 pulses of 200 ms followed by a continuous feed of hydrazine for 200 s, a lower amount of fine particles 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%). These data are linked to the refractory character of the carbide. In following work, the reactor will have to be optimized for the new catalysts, as it was for the Ir catalyst.

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