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DECOMPOSITION OF HYDRAZINE BY TUNGSTEN OXYCARBIDES: THE INFLUENCE OF MACROPOROSITY AND MECHANICAL STRENGTH ON A 2 N MICROTHRUSTER ENGINE

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Abstract: The aim of this work was to prepare tungsten oxycarbides by Temperature Programmed Reaction (TPR), starting with previously molded macroporous tungsten oxide (WO_3). The tungsten oxycarbides were prepared by one of two different methods: direct carburization with CH_4/H_2 to obtain WC or preliminary formation of nitrides with NH_3 to obtain W_2N, followed by carburization to W_2C and WC with CH_4/H_2. Results suggested that the carburization of the W_2N was incomplete, resulting in an oxycarbonitride, or did not occur at all, with the end material being W_2N. From among the materials prepared, two catalysts were selected as a function of their mechanical properties, and their performances were compared with a 2 N microthruster using the Shell 405 commercial catalyst in the reaction of hydrazine decomposition.
Keywords: tungsten oxycarbide, macroporosity, mechanical strength, hydrazine.

INTRODUCTION

Most satellites now use hydrazine decomposition microthrusters for maneuvering. This decomposition is usually attained on Ir/Al_2O_3 [Armstrong et al., 1978]. This reaction is extremely exothermic; it occurs in short time intervals (ms) and is controlled by heat and mass diffusion processes. As a consequence, two catalyst parameters are essential to the process: a pore volume between 0.25 and 0.50 cm^3g^{-1} with 50% of the pores having meso and macroporosity, which would facilitate the diffusion process of the gases generated in this reaction, and an acceptable mechanical strength, which would minimize the loss of mass due to catalyst fractures during microthruster operation. Once the catalyst bed is exposed to hydrazine, a pressure gradient from 0.1 to 20 bar may occur in a fraction of a second, while the temperature may reach 800°C in a few seconds.

Since the past decade, transition metal oxycarbides and oxynitrides have been studied as potential substitutes for noble metal catalysts [Leclercq et al., 1989 and Oyama, 1992]. These new catalysts have shown promising results in their use in satellite micropropulsion systems [Rodrigues et al., 1996]. Of those species studied, the tungsten oxycarbide catalyst showed the best performance [Rodrigues et al., 1997]. However, its distribution of pores was not the most suitable for use in micropropulsion systems, since it only had micro and mesopores.

Hence the objective of this work was to discuss the influence of the generation of tungsten oxycarbide macroporosity on the mechanical strength behavior of these materials and on the performance of microthrusters under altitude simulation test conditions, using hydrazine as the propellant.

EXPERIMENTAL

Oxycarbide synthesis reactions, prepared either by direct carburization or by preliminary formation of nitride, were performed with tungsten oxide (Labsynth, >99%). The first step was the molding of extruded tungsten oxide, comprising the dispersion, molding and drying of the tungstic acid powder samples [Vieira, 1997]. The macroporosity of the tungsten oxide was generated by controlling the variables which can alter the nucleation processes and particle growth during the initial precipitation step. Conditions found to be optimal for maximizing macroporosity in terms of heating rate and temperature as well as the required thermal treatments to achieve the proper mechanical strength for the precursor oxide were shown in a recent article [Vieira, 1999].

The formation of nitrides of the extruded macroporous tungsten oxide sample consisted of heating it from room temperature to 730° C at a rate of 1° C min^{-1} in NH_3 (Air Liquide, 99.4%) flow, and then maintaining it during 6h..

Carburization of the extruded macroporous tungsten oxide sample as well as of the oxynitride resulting from the nitride formation described above consisted in heating from 400°C to 700° C also at the rate of 1° C min^{-1} to obtain W_2C, and up to 880° C to obtain WC, both in a stream of 80% CH_4 (Air Liquide, 99.97%) in H_2 (Air Liquide, 99.999%). This carburization procedure followed three different paths: carburization to W_2C and WC via tungsten oxynitride (i.e. via nitride) and carburization to WC via tungsten oxide (i.e. direct).

Following these steps, the materials were reduced in H_2 at 700° C to W_2C and at 750° C to WC for removal of the excess carbon deposited on the catalyst surfaces. Finally, because these materials were pyrophoric, they were "passivated" by slow oxidation of the surface in a flow of 1% (v/v) O_2 (Air Liquide, 99.998%) in He (Air Liquide, 99.999%), thus avoiding an excessive temperature increase that could affect the product's texture and catalytic properties.

The final materials were characterized using X-ray diffraction (Phillips PW1830), mercury intrusion (Quantachrome Autoscan 33), nitrogen adsorption (Quantachrome NOVA 1000), mechanical strength response with respect to compressive loads on individual samples (Instron 4301), elementary chemical analysis (LECO TG436DR and CS-444) and Scanning Electron Microscopy (LEO 440).

The performances of these final materials were evaluated in a 2 N monopropellant hydrazine microthruster on a test bench in vacuum, as shown in Fig.1.

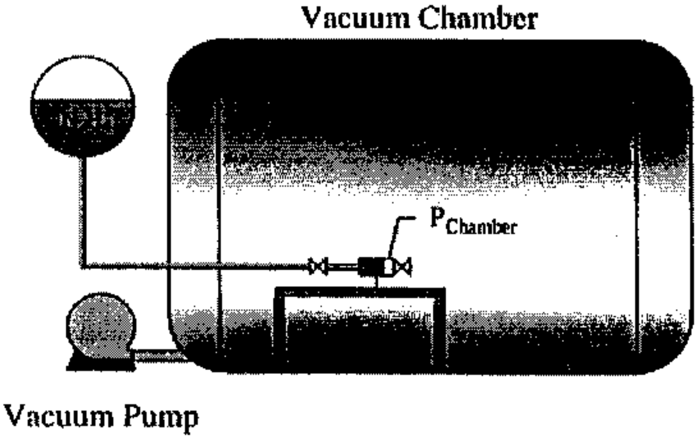

Figure1: Diagram of the bench test and propulsion system, where $P_{Chamber}$ is the stagnation chamber pressure.

RESULTS AND DISCUSSION

In the following discussion, the materials prepared via nitride will be represented as WC-*vn* and W_2C-*vn*, respectively, while the one prepared in the direct way will be designated as WC-*d*.

The X-ray diffraction results for the WC-*vn* and WC-*d* samples showed a structure corresponding to WC, while the W_2C-*vn* sample showed a structure corresponding to β-W_2N, which in the latter case indicated that carburization of the nitride did not occur.

From the results shown in Table 1, it can be seen that:

Table 1: Results of crystalline structure, specific area (S_g), pore volume (V_P) for pore diameter (d_P) >10 nm and mechanical strength (MS)

	Structure	V_P (cm^3g^{-1})	S_g (m^2g^{-1})	MS (N)
WO_3	orthorhombic	0,18	4	49
WC-vn	hexagonal	0,21	31	32
W_2C-vn	cubic	0,21	42	50
WC-d	hexagonal	0,21	21	3

Nitride formation and carburization reactions do not noticeably change the meso and macroporous volume (d_P> 10 nm) of the precursor oxide.

The specific areas of the carburization products, determined after passivation and slow oxidation of the surface, are compatible with those found in the literature for materials prepared with 80% CH_4 in an H_2mixture (v/v) [Ribeiro et al., 1991 and Iglesia et al., 1992], which is an indirect measurement of the existence of micropores and mesopores.

Tests dealing with the mechanical strength response to compressive loads showed that the tungsten carbide obtained by direct carburization of the oxide (WC-*d*) possessed much less mechanical strength than that obtained via nitride, discouraging its use in microthrusters. Mechanical strength is probably not affected by nitride formation, but it decreases during carburization.

The results of the elementary analysis shown in Table 2 point out that the WC-*vn* composition is in fact $WC_{0.68}N_{0.05}O_{0.63}$, while that corresponding to W_2C-*vn* is actually $W_2C_{0.65}N_{0.31}O_{1.37}$.

Table 2: Oxygen, nitrogen and carbon contents found after carburization of the tungsten oxynitride

Samples	O (% wt)	N (% wt)	C (% wt)
WC-vn	5.02±0.17	0.34±0.01	4.02±0.14
W_2C-vn	5.44±0.03	1.07±0.03	1.95±0.02

These results may indicate that carburization was incomplete in the case of WC-*vn*. Beacuse nitrogen removal was nearly complete, one can suspect that the high oxygen content in this material is due principally to the precursor oxide in the crystalline lattice, with the oxygen introduced by surface oxidation being responsible for a small fraction of it, as was seen by the low oxygen consumption during this last treatment. The Xray diffraction results for the W_2C-*vn* correspond to the β-W_2N phase. This is confirmed by the high level of nitrogen present after the carburization step. Hence, the carbon present in the chemical composition may be assumed to be a polymeric carbon layer covering the surface. In fact, reduction treatments under different conditions of temperature and time showed that the complete removal of this carbon layer is not an easy operation.

Ribeiro et al. (1991) and Iglesia et al. (1992) prepared WC, first starting with WO_3 and then W_2C, starting with β-W_2N with a carburizing mixture of CH_4 and H_2. Those authors also detected the presence of polymeric carbon on the surface of the catalyst as well as the existence of residual oxygen due to incomplete reduction of the precursor oxide.

Table 3 shows the results of three composition analyses, in percentage per element, obtained by Energy Dispersive X-ray (EDX) microanalysis for each material, while the corresponding figure (Fig. 2) shows the location of the points of analysis for the extruded and sliced samples of WC-*vn* and W_2C-*vn*.

Table 3: Percentages of oxygen, carbon and tungsten obtained by EDX

Micro-probe	WC-vn			W_2C-vn		
	O	C	W	O	C	W
1	9.2	27.2	63.6	11.6	28.8	59.6
2	9.0	30.9	60.1	11.3	31.5	57.2
3	11.5	41.4	47.1	12.8	39.7	47.5

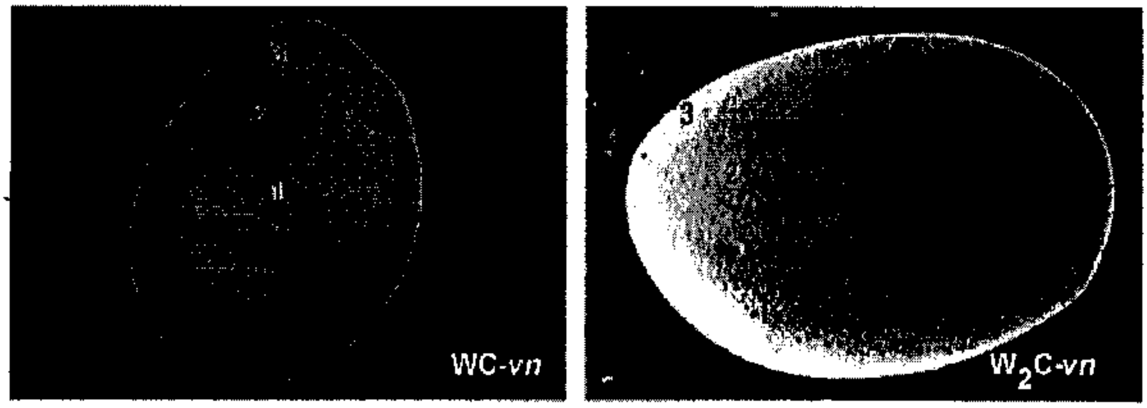

Figure 2: Images of the extruded samples of WC-*vn* and W_2C-*vn* obtained by secondary electron microscopy (SEM) with an EDX microprobe

Upon examining Table 3 one can verify that, for both samples studied, there was an accentuated decrease in the percentage of carbon atoms from the rim to the center of the extruded specimen. This result suggests that the materials have a heterogeneous composition as a function of the location of the points examined. This is an indication of a greater difficulty in carburization as one goes from the rim to the center of the extruded specimen, certainly owing to diffusion problems. These problems are probably due to the excessive use of a carburizing mixture rich in methane (80% CH_4 in H_2). The decrease in this percentage of carbon from the rim to the center of the extruded specimen, verified in all the samples examined, is a confirmation of the difficulty in substituting the nitrogen and also the oxygen in the lattice by the carbon, certainly caused by diffusion problems, suggesting that the conditions of carburization must be studied in greater depth.

An identical examination of the results corresponding to the percentage of oxygen atoms indicates that this parameter remains nearly constant, regardless of the position of the microanalysis points (microprobe), which could confirm the hypothesis that a reasonable amount of this oxygen coming from the precursor oxide is still part of the crystalline structure of the studied materials.

The EDX results of punctual analyses (shown in Fig. 2) did not offer evidence of the presence of nitrogen, unlike the results obtained by chemical analyses. According to chemical analysis the composition of WG*vn* was $WC_{0.68}N_{0.05}O_{0.63}$. This is acceptable, given the low level of nitrogen in the samples, which is probably under the EDX detection limit.

In the case of W_2C-*vn*, whose chemical analysis composition corresponded to $WC_{0.33}N_{0.16}O_{0.69}$, the nitrogen level, despite being higher, could not be detected. In this case the hypothesis that the peak of nitrogen was masked by adjacent peaks, such as those of the carbon and of the oxygen, cannot be discarded.

The topographies of surfaces cut from extruded WC-*vn* and W_2C-*vn*, obtained by SEM, in some cases show, cracks, possibly caused by tensions generated during the preparation of the catalyst, mainly in the extrusion process and thermal treatments (Fig. 2). The existence of cracks is highly undesirable as this can lead to larger fractures and a consequent loss of catalyst during operation of the microthruster due to the high pressures and temperatures inside the pores.

Comparing the performances of WC-*vn* and W_2C-*vn* with that of the commercial catalyst, Shell 405 (30% Ir/Al_2O_3), in the same 2 N microthruster, we opted for conducting the tests under identical conditions, i.e. 100 pulses of 0.5 s at intervals of 0.5 s, starting with a temperature of 150°C and an injection pressure of 22 bar .

To simplify the comparison of the materials used in the microthruster, Table 4 shows some physical characteristics of the catalysts before the tests, i.e. mechanical resistance to compression (MS), medium diameter of the extruded material (d), total pore volume (V_P) and specific area (S_g).

Table 4. Physical characteristics of the catalysts tested in the 2 N microthruster

	MS (N)	d (mm)	V_P (cm^3g^{-1})	S_g (m^2g^{-1})
W_2C-vn	50	1.6	0.21	42
WC-vn	32	1.6	0.21	31
Shell 405	>100	0.6	0.15	115

According to reports of the Air Force Rocket Propulsion Laboratory [Petty, 1973], the most important criterion in the evaluation of catalysts, as far as their use in microthrusters is concerned, is the stability of the pressure generated in the stagnation chamber by hydrazine decomposition during the tests. Initial high peaks (spiking) with pressures above 50% of the mean stagnation pressure are undesirable, as are pressure instabilities greater than 10% of this pressure.

Figures 3 to 5 show the behavior of the catalyst Shell 405 commercial catalyst, WG*vn* and W_2C-*vn* when tested in microthrusters under pulsed regime. A comparison of these three illustrations shows that the Shell 405 commercial catalyst had the shortest response time (50 ms), followed by WC-*vn* (95 ms) and W_2C-*vn* (170 ms). The response time in this work is defined as the interval of elapsed time from the opening of the injection valve at the first pulse until the pressure of the stagnation chamber reaches the maximum value of the first peak. The increase in response times shown by WC-*vn* and W_2C-*vn* can be partly attributed to their possibly lower level of activity as well as to the differences in their granulometry and the densities of their beds.

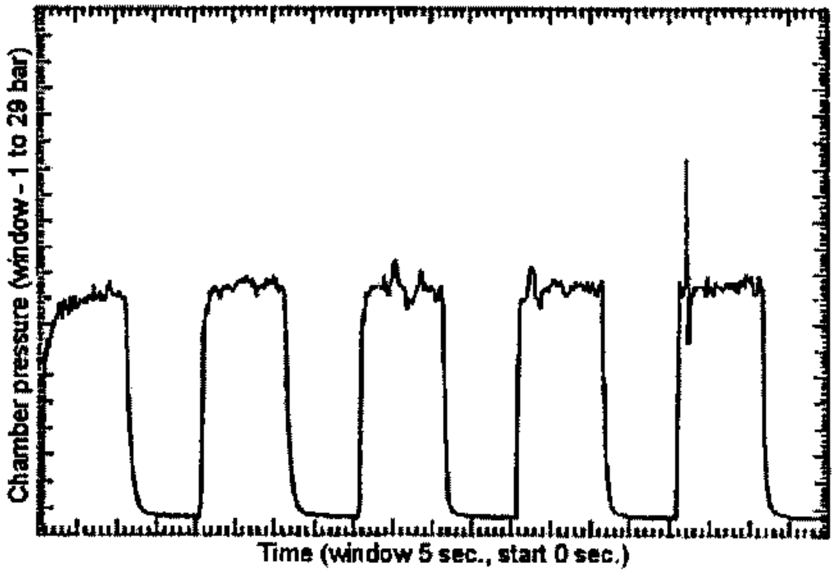

Figure 3: Performance of the Shell 405 commercial catalyst in a 2 N microthruster.

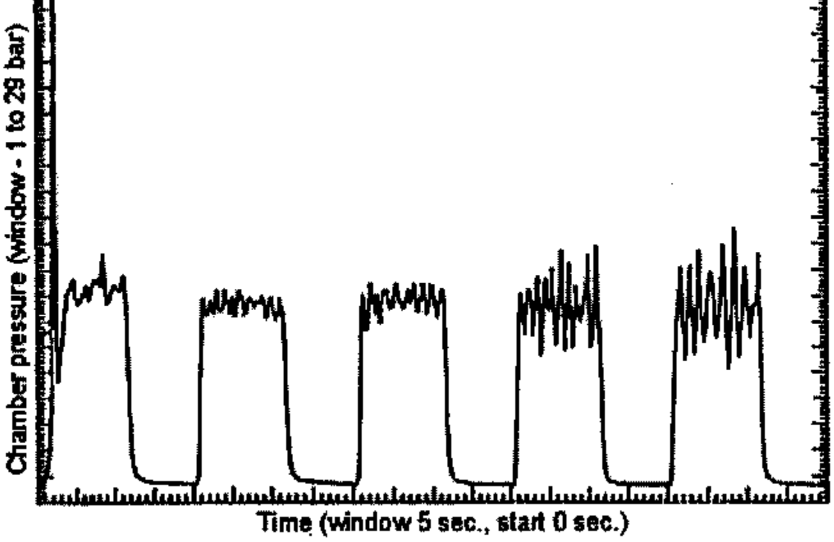

Figure 4: Performance of the WC-*vn* catalyst in a 2 N microthruster.

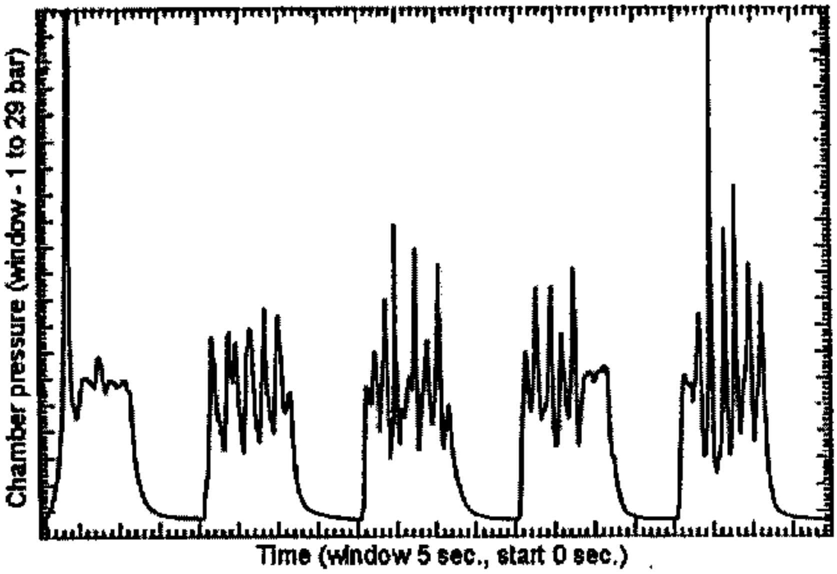

Figure 5: Performance of the W_2C-*vn* catalyst in a 2 N microthruster.

The intensity of the initial peak during the first pulse is extremely high for WC-*vn* (50 bar) and W_2C-*vn* (52 bar), while in the case of the Shell 405 commercial catalyst, this intensity was shown to be lower than (11 bar) the mean stagnation pressure (14 bar). These overpressures corresponding to the first peak are probably caused by the condensed hydrazine which accumulated inside the pores of WC-*vn* and W_2C-*vn* due to the longer response times at the beginning of the reaction. These overpressures certainly are the main cause of the brittleness of WC-*vn* and W_2C-*vn*, which led to the partial powdering of the catalytic bed, greater instability of the chamber pressure in pulsed tests and the early alterations of these two materials during the tests.

CONCLUSIONS

Regarding the carburization reactions of tungsten oxide and oxynitride under the conditions established in this work, it can be concluded that:

1. mechanical strength is probably not affected by the formation of nitrides, but it decreases during carburization;

2. carburizations via nitride resulted in materials with the compositions $WC_{0.68}N_{0.05}O_{0.63}$ and $W_2C_{0.65}N_{0.31}O_{1.37}$, which correspond to WC-*vn* and W_2C-*vn*, the materials initially desired. These results, added to those obtained by X-ray diffraction, allow one to conclude that for WC-*vn* carburization was incomplete and for W_2C-*vn* it did not occur, possibly due to synthesis conditions such as heating rate, time of reaction and gas mixture composition. The high levels of oxygen can be due to the presence of this element in the crystalline lattice, even after the formation of nitrides and carburization, and also to the surface oxidation caused by the passivation, as became evident by the gains in mass during this treatment;

3. the EDX results showed an accentuated decrease in carbon level from the rim towards the center of the extruded samples. This was probably due to diffusion problems during carburization. It has also been demonstrated that the compositions of the samples were not homogeneous, and the phenomenon of diffusion could also explain the presence of nitrogen after carburization;

4. nitride formation as well as carburization do not appear to significantly alter the volume of pores with $d_p > 10$ nm or their distribution in the extruded precursor oxide; nevertheless these treatments generated a reasonable quantity of micropores ($d_p < 10$ nm), as can be seen by the increase in specific surface area; and

5. the images obtained by SEM showed the existence of cracks in some of the extruded samples obtained by carburization via nitride, whose mechanical strength was considered satisfactory. The presence of cracks is one of the main causes of powdering and of catalyst loss of mass during the tests with hydrazine decomposition in the microthruster.

The main conclusions obtained from the tests with a microthruster were the following :

1. for materials with a lower level of specific activity during hydrazine decomposition than that of the Shell 405 commercial catalyst, the most critical preparation parameter is achievement of high mechanical strength, even with the loss of macropore generation, and

2. an excessive overpressure during the first pulse can result in brittleness of the sample and loss of mass, which is of extreme importance for materials with a lower mechanical strength.

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