

Burning Stability of Composite Solid Propellants Including Zirconium Carbide

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This work examines the effect of zirconium carbide as an additive for the stable combustion of composite solid propellants based on hydroxy-terminated polybutadiene, some of which include iron (III) oxide as a burning rate catalyst, with different solid loadings, fraction mixtures and particle sizes of ammonium perchlorate. Viscosity values, mechanical characteristics (the maximum stress and strain at the maximum load) and the burning rate law at two extreme test temperatures were determined and calculated at room temperature using temperature sensitivity values for each of 12 propellants

Key words: composite rocket propellant, combustion, combustion stability, zirconium carbide.

Introduction

ONCE the grain is ignited, thrust cannot be stopped. The grain will burn at a set rate until all propellant is consumed. However, unstable combustion usually occurs in tests of rocket motor containing propellant composition limits, in the case of high calorific values or with a high specific impulse of propellant. That is the case with composite rocket propellants (CRP) based on ammonium perchlorate (AP) as an oxidizer, and also with compositions with a high share of binders. While some propellants do not show these characteristics, the others almost always, even during grain combustion, undergo extreme temperatures.

For improving ballistic performances and damping unstable combustion, the compounds of elements of group II (calcium, magnesium, zinc, cadmium, mercury), group III (boron, aluminium) and group IV of the periodic system (silicon, titanium, zirconium, antimony, lead) are often used. This paper will show the effect of zirconium carbide [1].

Theoretical part

Rockets operate on the principle of Newton's third law of motion that "for every action there is an equal and opposite reaction". The propellant combustion results in the formation of hot gases which are accelerated at high velocity through a nozzle. The propellant is molded into a solid shape inside the rocket motor. On ignition, a chemical reaction occurs between the fuel and the oxidizer which produces hot gases required to produce thrust [2].

An unstable combustion occurs when an existing working pressure in the motor chamber rises above the value for which the observed motor is designed. It is characterized by fluctuations in the value of the pressure in some parts or in the whole working range (average pressure is above the assumed value), with a sudden increase in the chamber pressure that could produce catastrophic

consequences for the motor [3]. An example is shown in Fig.1 [4].

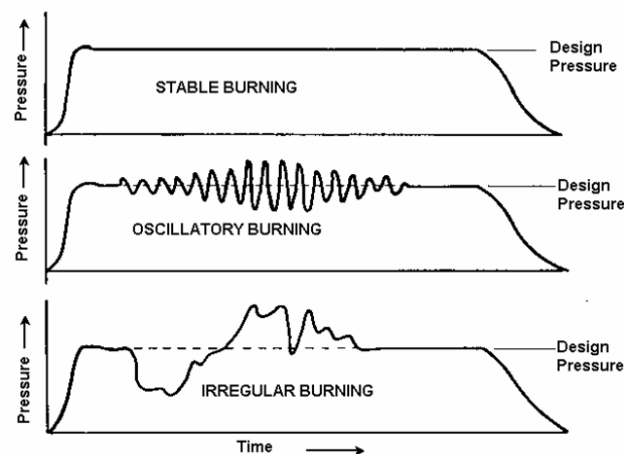


Figure 1. Normal and unstable combustion of propellants

If the pressure is higher than expected, the motor cannot be used with acceptable reliability, as the ballistic performance varies depending on the thrust - time change and it is obtained from the pressure change with time [5].

Various factors influence the occurrence of unstable combustion and it happens when a rocket motor works at a higher pressure or it has a greater length or length to diameter ratio, or it is embedded with a propellant with a larger content of the solid phase (oxidizer) or when it works at elevated temperature.

The CRP structure is heterogeneous, and so is the combustion wave structure. Even when the particle size of AP is 10 μm (or less), it is very large compared to the size of molecules [6]. AP particles on the propellant surfaces are decomposed creating gaseous fragments that react with gases occurred by separation of the polymer binder.

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Gasification at the surface means the presence of unbound or broken polymer chains forming a mixture of monomeric units and chains of different size fragments [7]. The mixing of gaseous oxidizer and binder products has a very important role in the combustion process. The rate of binder and oxidizer consumption is determined by the rate of their expansion in the area where they meet and react.

The thickness of the reaction zone is reduced by a higher operating pressure. Spectrographic studies showed that the thickness of the gas flame during the combustion of the CRP area is about 100 μm at 1-5, but at higher pressures (above 70 bar), the reaction zone is located very close to the AP crystal surface and the thickness of this layer is only 0.5 μm [8].

Combustion instability may occur as a result of inefficient mixing of the components of the gas flame zone. The thermodynamic temperature of the combustion products is usually 2000 - 3000 K and the combustion temperature of the propellant surface is 500-700 K. Therefore, a very large temperature gradient occurs in the combustion zone [9].

The temperature of the propellant will affect the reaction rate of the propellant ingredients and thus the burning rate. Between the operating range of 244 K (-29°C) and 344 K (71°C) typical composite propellants will experience a 20 to 35% variation in the chamber pressure and a 20 to 30% variation in the burn time [2].

The temperature effect on propellant burning is given in Fig.2, where three working temperatures are shown (160°F = 71°C, 70°F = 21°C and -65°F = -54°C) [4].

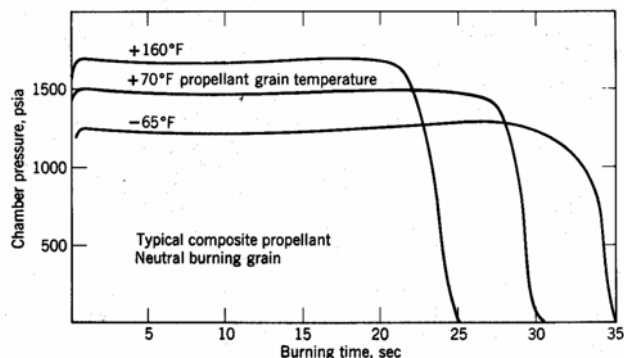


Figure 2. The temperature effect on propellant burning

Burning rate depends on a number of factors including particle size, particle shape, grain configuration, chamber pressure and oxidizer (or total solid phase) percentage. Elemental laws and burning rate equations usually deal with the influence on some of the important parameters individually. It is often possible to approximate burning rate as a function of chamber pressures over a limited range of chamber pressures.

The relationship between the rate and the pressure of propellant combustion in the motor chamber, i.e. linear speed limits change between solid propellant and gaseous products of its combustion, has been given by the burning rate law (Saint-Robert law):

$$v = B \cdot p^n$$

or

$$\log v = n \log p + \log B \quad (1)$$

where is:

v – burning rate,

p – working pressure in the motor chamber,

B – const.,

n – pressure exponent.

„ B “ is known as the temperature coefficient and is non-dimensional. It is influenced by the ambient temperature of the grain. The burning rate exponent „ n “ is independent of the grain temperature and describes the influence of the chamber pressure on the burning rate. High values of „ n “ give a rapid change of the burning rate with pressure which means that even a small change in pressure will result in a substantial change in produced hot gases. So, the pressure exponent value is accepted as a measure of burning rate sensitivity to the change of propellant pressure and this value decreases as the exponent value approaches zero.

If the propellant has a steady performance in the range of -50°C to +75°C, then, by increasing the ambient temperature, the burning rate, the pressure exponent and the pressure in the chamber will rise.

The CRP burning rate significantly depends on its initial temperature. The temperature sensitivity of the burning rate is the consequence of the temperature effect on all processes in the mechanism of combustion and is given as [7]:

$$\sigma_p = \frac{\ln(v_2/v_1)_p}{T_2 - T_1} \quad (2)$$

where:

v_2 - burning rate at the pressure » p « and the temperature T_2 (mm/s),

v_1 - burning rate at the pressure » p « and the temperature T_1 (mm/s);

where $T_2 > T_1$, and

p - working pressure value in the chamber corresponding to the burning rates v_1 and v_2 , (bar).

The values of instability and a significant increase of the exponent pressure indicate a so-called critical pressure [10].

It is important to note that if the used propellant is particularly sensitive to pressure increase, burning will get out of control and could possibly lead to an explosion. For this reason, it is recommended that a propellant with a constant burning rate over a range of pressures is used.

There are different methods of solving problems of instability when it is a result of propellant composition.

Some of them consist of adding metal powder which, during combustion, transforms into oxides.

The presence of such additives in a relatively small amount (0.3 - 3.5%), and even less than 2%, extends the range of the stable combustion of CRP and the critical pressure moves to higher values [1, 11]. High values of the heat capacity and thermal stability of propellants indicate that these metal particles play the role of "thermal leakage" in the zone of the combustion of propellant foaming, and this leads to a shift of the critical pressure to a higher value. The influence of the compounds of the elements from groups II, III and IV of the periodic system increases by reducing the diameter of the powder particles, preferably less than 15 μm .

In this paper, the level of zirconium compound influence will be shown regarding temperature sensitivity.

Experimental part

Eleven different compositions of CRP have been examined: various ratios of bimodal and trimodal oxidizer fractions, oxidizers particle sizes, different solid particles content and compositions including iron (III) oxide (Fe_2O_3)

as a burning rate catalyst. The view of this type of "red color" propellant is shown in Fig.3.



Figure 3. Uncured propellant with Fe₂O₃

All the compositions are shown in Tables 1, 2 and 3.

Table 1. Bimodal compositions (200/10)

Batch	AP-200, (%)	AP-10, (%)	ZrC, (%)	AP _{tot.} , (%)	TSP*, (%)
86	66.56	16.64	0.8	83.2	84.0
105	39.75	39.75	0.5	79.5	80.0
106	50.0	30.0	0.5	80.0	80.5

*TSP (total solid phase)

Table 2. Bimodal compositions (200/10) with Fe₂O₃

Batch	AP-200, (%)	AP-10, (%)	ZrC, (%)	Fe ₂ O ₃ , (%)	AP _{tot.} , (%)	TSP*, (%)
104	40.5	40.5	0.4	1.2	81.0	82.6
116	55.0	24.0	0.5	0.5	79.0	80.0
118	67.2	16.8	0.6	0.3	84.0	84.9
120	49.5	33.0	0.6	0.3	82.5	83.4

Table 3. Bimodal (200/80) and trimodal (200/80/10) propellant compositions

Batch	AP-200, (%)	AP-80, (%)	AP-10, (%)	ZrC, (%)	AP _{tot.} , (%)	TSP*, (%)
89	60.4	14.8	-	0.8	75.2	76.0
103	62.4	15.6	-	0.8	78.0	78.8
107	18.0	32.0	29.3	0.5	79.3	79.8
109	22.0	34.3	21.5	0.5	78.3	78.8

The CRP has been based on hydroxy-terminated polybutadiene (HTPB) and isophorone-diisocyanate (IPDI) as a curing agent, including other ingredients such as oxidizers, plasticizers, bonding agents, and antioxidants. The propellant has been homogenized in a vertical mixer bowl at 50°C. Because of decreasing the shear stress and slowing the curing rate reaction, the abatement of the mixing temperature was desirable. Some of the compositions are susceptible to viscosity increase due to the presence of metal (Fe and Zr) ions [1, 12].

Afterwards, the propellant is cast into the chambers of the experimental motors (Fig.4) and into the moulds for all other test specimens (Fig.5). All specimens were cured at (70±2)°C.



Figure 4. Experimental motors of 2 inches



Figure 5. Cured blocks of propellant for all other test specimens

Results of examinations

The viscosity changes during the curing time (every 15 minutes) have been determined with a Brookfield viscometer, type HBT, at (50±2)°C. The graphic results are shown in Fig.6 (higher values) and Fig.7 (lower values), all in Pa x s.

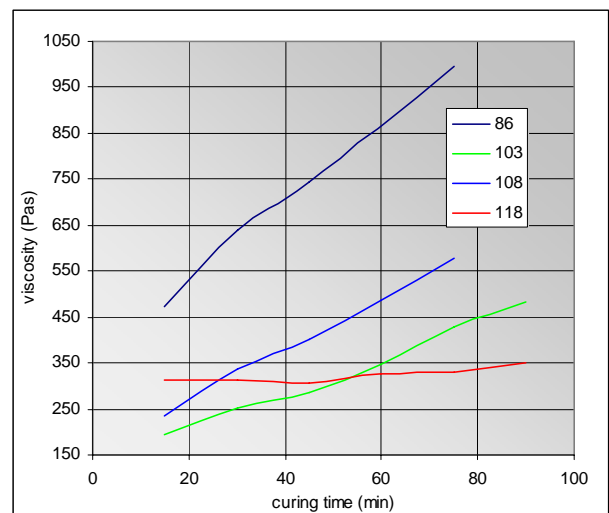


Figure 6. CRP with higher viscosity values

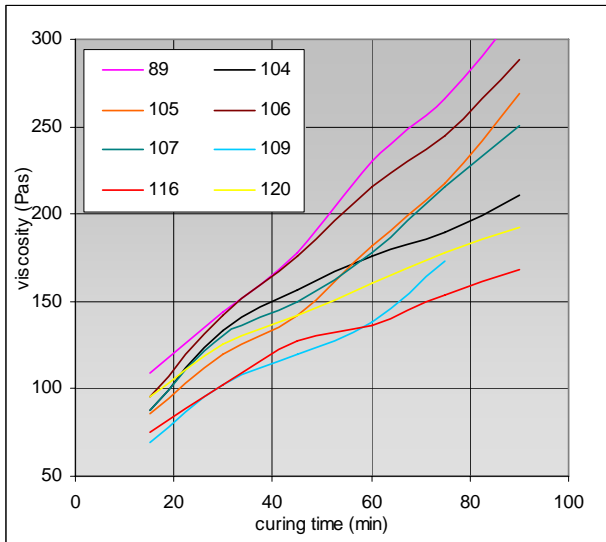


Figure 7. CRP with lower viscosity values

The mechanical characteristics are determined by the uniaxial tensile test at $(20 \pm 2)^\circ\text{C}$ and a crosshead speed of 50 mm/min. The graphic results of two calculated characteristics are shown in Fig.8 (tensile stress, daN/cm²), and Fig.9 (strain at maximum load, %).

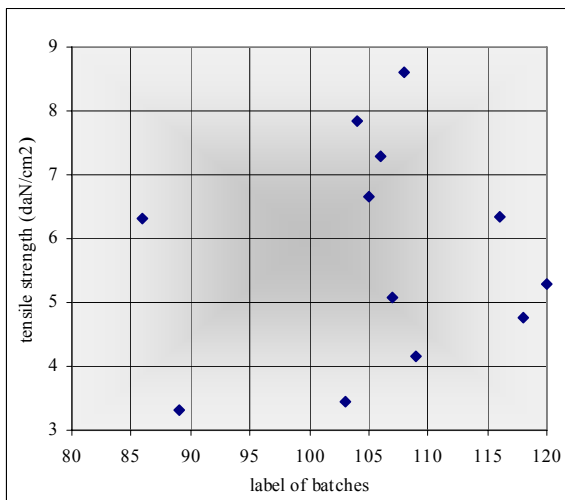


Figure 8. Tensile stress values for the numbered batches

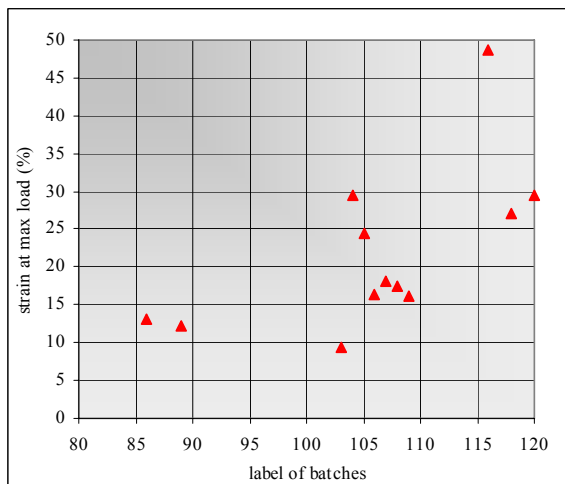


Figure 9. Strain at maximum load values for the numbered batches

From each cast batch of propellant, the static tests have been performed for determining the parameters in the burning rate law at two temperatures (-40°C and 50°C).

The two calculated parameters from the burning rate laws are shown in Tables 4 and 5:

- burning rate at 70 bar (v_{70}), and
- pressure exponent (n)

have been determined at test temperatures (-40°C and 50°C).

Table 4. Burning rate parameters calculated at -40°C

Batch	v_{70} (mm/s)	n
986	8.18	0.2801
989	5.87	0.3287
103	7.23	0.4050
104	15.61	0.4127
105	7.15	0.3980
106	7.24	0.3963
107	7.85	0.4364
108	8.87	0.4159
109	6.91	0.3085
116	10.39	0.4623
118	10.48	0.4569
120	11.04	0.4806

Table 5. Burning rate parameters calculated at 50°C

Batch	v_{70} (mm/s)	n
986	9.34	0.2696
989	7.12	0.3124
103	8.48	0.5013
104	16.70	0.3467
105	8.49	0.4635
106	8.40	0.3486
107	9.11	0.4602
108	10.54	0.5144
109	8.30	0.4238
116	11.70	0.4242
118	11.96	0.4830
120	12.34	0.5055

The values of the temperature sensitivity (σ_p), calculated from equation (2) at the working pressure (70 bar) are given in Table 6. Also, the same table shows the corresponding values of π_k (pressure sensitivity) calculated from the next equation:

$$\pi_k = \frac{\sigma_p}{1-n(3)} \quad (3)$$

Table 6. Temperature and pressure sensitivity values

Batch	σ_{70} (%/ $^\circ\text{C}$)	π_k (%/ $^\circ\text{C}$)
986	0.1471	0.2014
989	0.2158	0.3138
103	0.1763	0.3535
104	0.0750	0.1148
105	0.1918	0.3575
106	0.1659	0.2547
107	0.1651	0.3058
108	0.1918	0.3949
109	0.2034	0.3530
116	0.1320	0.2292
118	0.1463	0.2830
120	0.1245	0.2518

Discussion

A comparison of the combustion stabilizer efficiency can be evaluated in the same propellant formulation where aluminium or ZrC was added.

The effectiveness of Al, observed by temperature sensitivity of some previously made compositions with and without a stabilizer, is presented first. In all cases, the parameters of the burning rate law are calculated at 20°C using the same values obtained at -40°C and 50°C and using the calculated values of the temperature sensitivity from equation (1).

The two batches with and without Al are shown in Table 7, as an example of the Al effect and the corresponding graphs in Figs.10 and 11.

Table 7. Compositions with Al and without any stabilizer

Batch	AP 200, (%)	AP 80, (%)	AP 10, (%)	Al (1530)	AP _{tot.} , (%)	TSP*, (%)
221	62.4		15.6	3+3	78.0	84.0
239	60.8	15.2		-	76.0	76.0

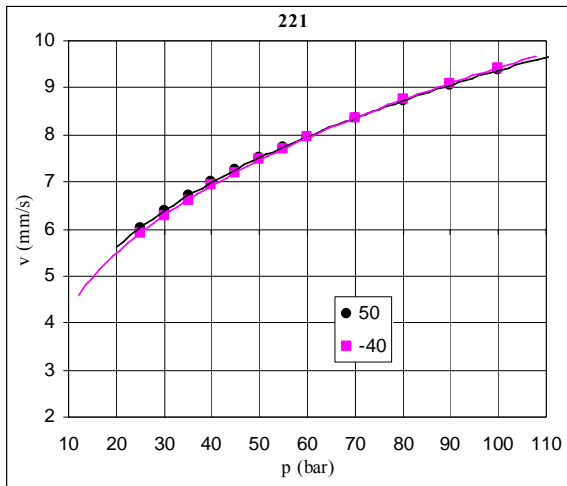


Figure 10. Burning rate law of 221 at 20°C

Batch 221 contains 6 % of Al and bimodal (200/10) AP. It can be seen that the curves coincide, while the same ones, calculated for a formulation without a stabilizer, show significant deviations of the calculated values at two temperature values.

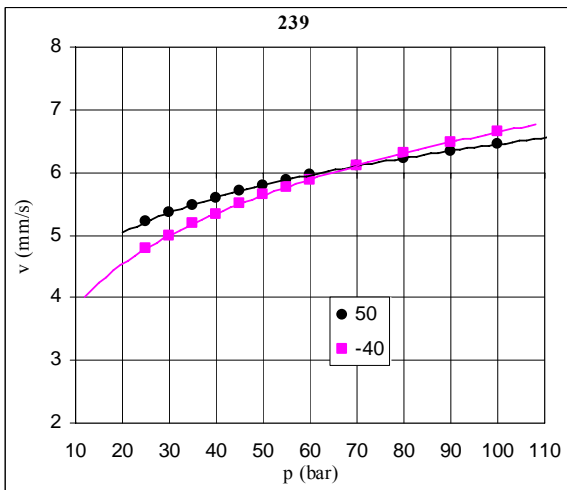


Figure 11. Burning rate law of 239 at 20°C

The same amount of Al has no equal effect on the composition of different fractions of AP. It means that in a

composition of the same AP fractions, the increase of Al increases the matching of curves.

Analog compositions including ZrC ($d=3,15 \mu\text{m}$), from Tables 1, 2 and 3 will show different matching levels of the calculated burning rate laws.

No 986 and 989 are analogue to those from Figs.10 and 11, as it can be seen in Table 8 and are plotted in Figs.12 and 13.

Table 8. Pairs with Al, ZrC and without any stabilizer

Batch	AP, (%)	TSP*, (%)	AP ₂₀₀ /AP ₁₀	AP ₂₀₀ /AP ₈₀	Al, (%)	ZrC, (%)
221	78.0	84.0	80/20		6	
986	83.2	84.0	80/20			0.8
239	76.0	76.0		80/20		
989	75.2	76.0		80/20		0.8

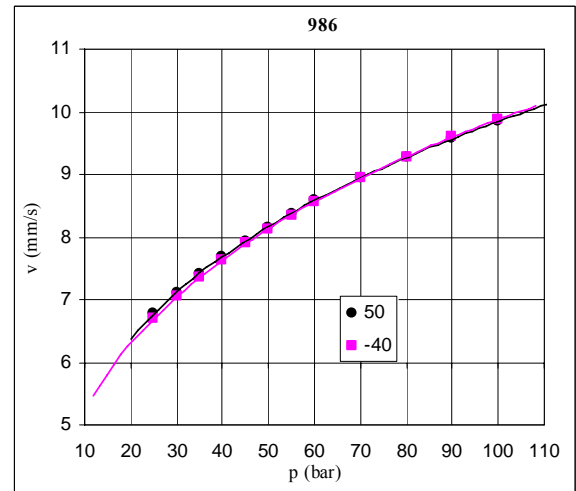


Figure 12. Burning rate law of 986 at 20°C

A positive effect of ZrC may be observed in both cases: in the first case, it successfully replaces Al and in the second case, the composition is sufficiently stabilized by the used amount.

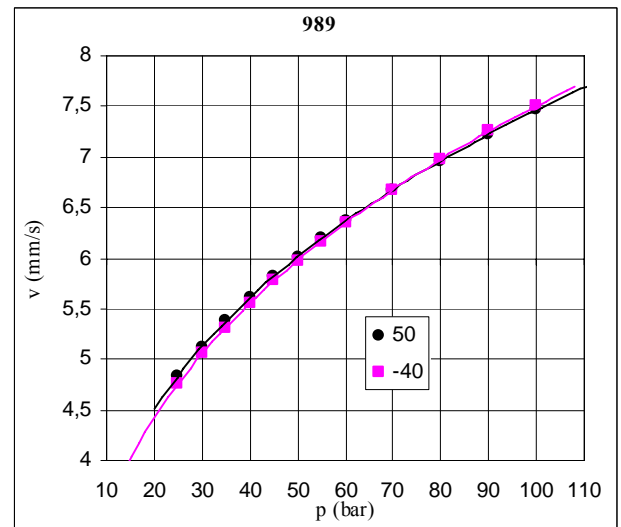


Figure 13. Burning rate law of 989 at 20°C

No 103 is analogue to No 989, while including a greater share of AP in the same fractions ratio AP₂₀₀/80=80/20. This propellant structure requires amounts of ZrC greater than 0.8% for the successful stabilization. This fraction combination is considered one of the most unfavorable and undesirable for a stable combustion process.

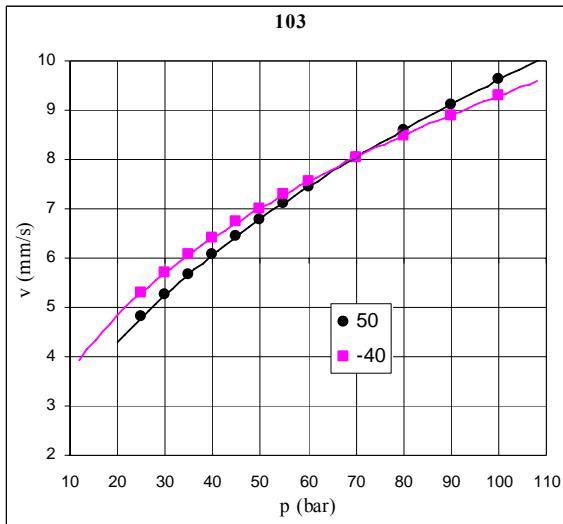


Figure 14. Burning rate law of 103 at 20°C

The examination of No 986 showed that the content of 0.8% of ZrC is optimal for the fraction combination of AP200/AP10=80/20. However, when the same fractions are used in a ratio from 40/60 to 65/35, in a total AP content up to 82.5%, the used quantity of 0.4 - 0.5% of ZrC was insufficient as a lower limit. Mutual deviations are obvious in Figs.15-17.

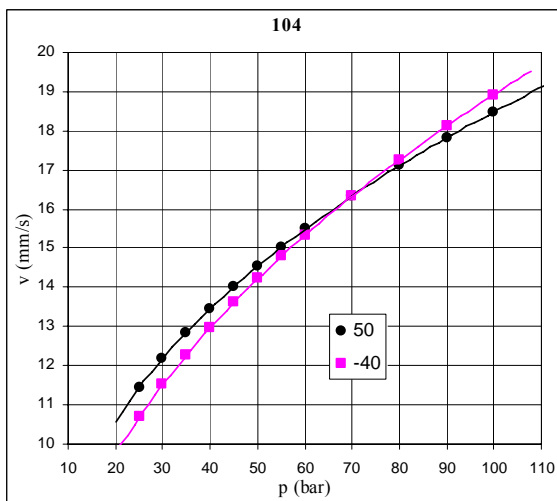


Figure 15. Burning rate law of 104 at 20°C

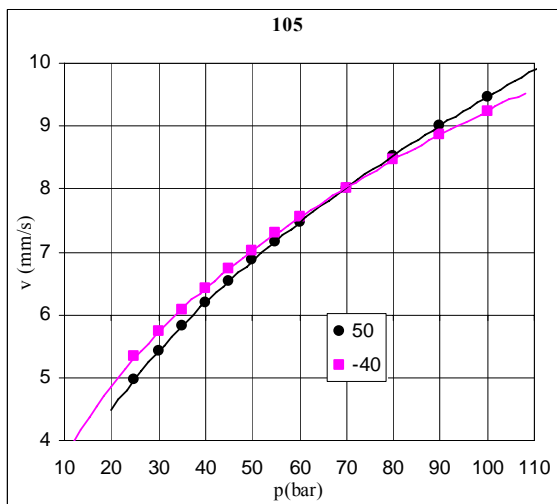


Figure 16. Burning rate law of 105 at 20°C

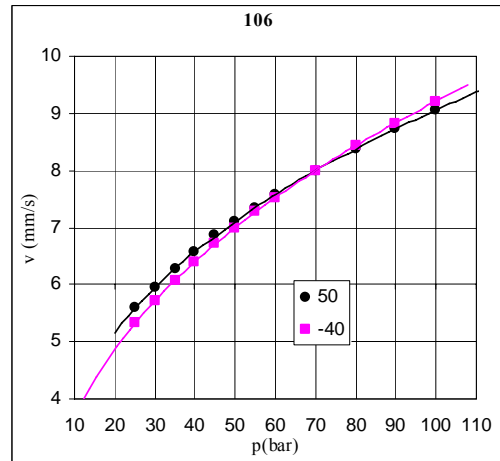


Figure 17. Burning rate law of 106 at 20°C

The stabilizer quantity for No 116 is on the very limit for the AP fraction ratio 70/30 and a total AP content of 79.0% taking into account the presence of ferric(III)-oxide as a burning rate catalyst which has the opposite effect from a stabilizer. The same conclusion applies for No 104 (Fig.15).

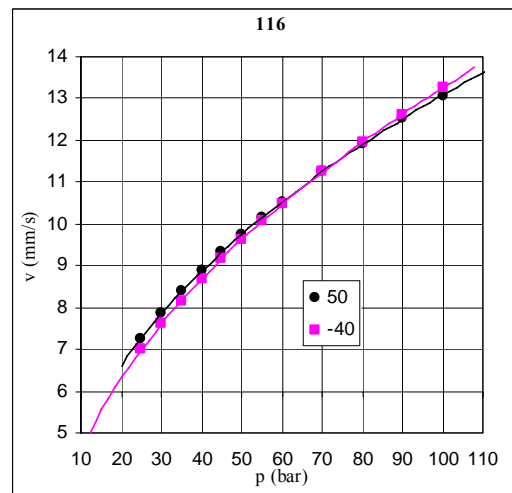


Figure 18. Burning rate law of 116 at 20°C

A slight ZrC increase to 0.6%, in the presence of the burning rate catalyst and the fraction ratio of AP200/AP10 from 60/40 to 80/20 provides stable combustion including a total AP content range from 79 to 84%.

These are batches No 118 and No 120 in Figs19 and 20.

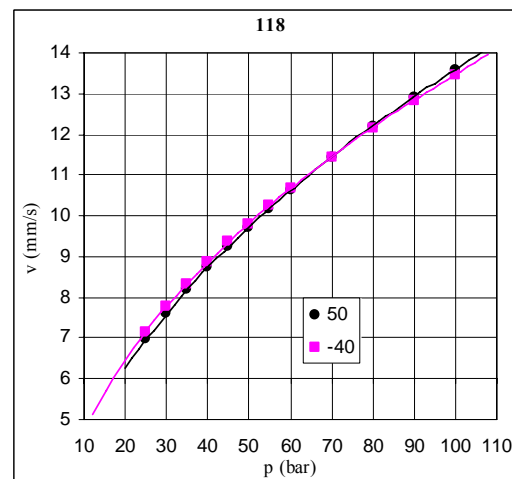


Figure 19. Burning rate law of 118 at 20°C

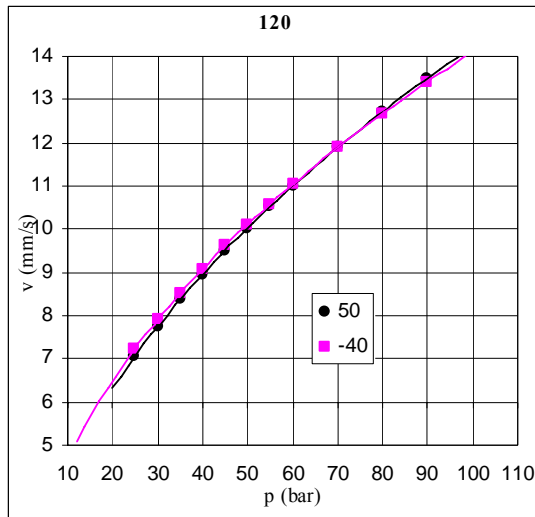


Figure 20. Burning rate law of 120 at 20°C

What happens with the propellants including trimodal oxidizer mixtures can be observed from batches No 107 and No 109, shown in Figs. 21 and 22.

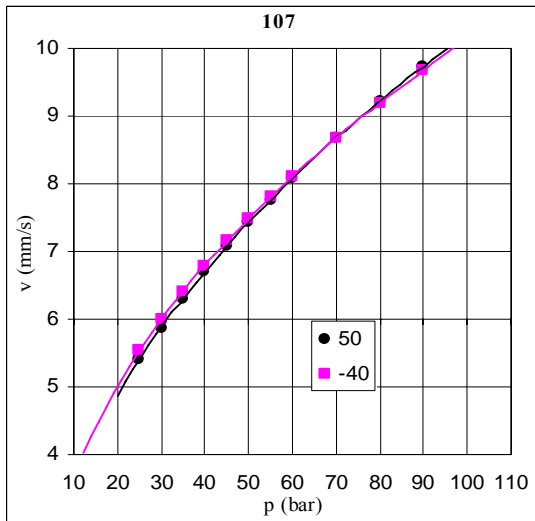


Figure 21. Burning rate law of 107 at 20°C

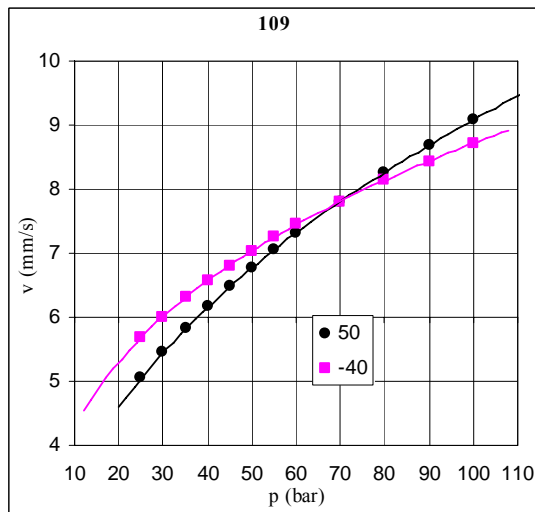


Figure 22. Burning rate law of 109 at 20°C

In both cases, the same quantity of ZrC is used for the stabilization of the burning process, but the final appearance is quite different.

It has been confirmed that a higher combustion stability is obtained in the compositions including the lower share of the coarsest AP particles (in this case, 200 μm), where the trimodal fractions are mixed, such as in No 107 with 18% of this type of AP. Only 0.5% of ZrC was added in this formulation.

On the other hand, for better particle packing, it is desirable that the share of the finest fraction (in this case, 10 μm) is larger than 1/3. As a consequence, the curves for No 109 do not show a superposition.

Conclusion

The research of the development of composite solid propellants has been based on hydroxy-terminated polybutadiene including zirconium-carbide as an additive for stable combustion of these types of propellants.

Eleven bimodal and trimodal ammonium-perchlorate fraction compositions have been prepared with different solid loadings, fraction mixtures and particle sizes of ammonium perchlorate, some including iron (III) oxide as a burning rate catalyst and with a different quantity of ZrC. Viscosity values, mechanical characteristics (maximum stress and strain at the maximum load) and the burning rate law at two extreme test temperatures have been determined and calculated at a room temperature using temperature sensitivity values at 70 bar for each batch of propellants.

Two independently obtained curves of the burning rate laws at 20°C (one from -40°C and temperature sensitivity and the other from 50°C and temperature sensitivity) were compared by the degree of superposition (or as a level of deviation).

When a match of curves is satisfactory, it is considered that the composition shows a good characteristic of combustion, i.e. it burns steadily and vice versa.

Based on the examined compositions, the following conclusions have been drawn:

- for the stabilization of the propellant using a bimodal AP mixture of 200/10 μm , for all technically feasible fraction ratios (from 50/50 to 80/20), the quantity of 0.5% - 0.8% of ZrC is quite enough; for a lower fraction ratio, it takes more ZrC within a given range;
- for the stabilization of the propellant using a bimodal AP mixture of 200/80 μm , 0.8% of ZrC is not enough; the same formulation with 6% of Al is unstable as well;
- for the stabilization of the propellant using a trimodal AP mixture of 200/80/10 μm , it is very important to take care of the coarsest fraction (it needs to be at the minimum level) and the finest fraction contribution (which should be included with 1/3 of the total AP) in order to determine the optimum amount of the stabilizer; in any case, 0.5% of ZrC is the lowest content for these types of propellants.

The application of ZrC instead of aluminium is very useful because of aluminium-trioxide (Al_2O_3) particles formed by Al combustion. Due to an undesirable process of precipitation, these particles accumulate on the rocket motor nozzle causing its erosion.

The effect of ZrC on the stable combustion of composite solid propellants is very advantageous which was noticeable during the examinations presented in this paper. Finally, it is easily possible to determine the required quantities of ZrC as a useful alternative combustion stabilizer.

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Stabilnost sagorevanja kompozitnih raketnih goriva sa cirkonijum-karbidom

U radu je prikazano istraživanje uticaja cirkonijum karbida kao aditiva za stabilno sagorevanje kompozitnih raketnih goriva na 12 različitih sastava na bazi hidroksiterminiranog polibutadiena, gde su neki od sastava sadržali gvožđe (III) oksid kao katalizator brzine sagorevanja, različitih udela čvrstih faza, udela frakcija oksidatora i veličina čestica amonijum-perhlorata. Merene su promene vrednosti viskoziteta tokom vremena umrežavanja i vrednosti zatezних čvrstoća i izduženja pri maksimalnoj sili testom jednoosnog zatezanja na sobnoj temperaturi, kao i zakoni brzine sagorevanja na dve ekstremne temperature, na osnovu kojih su izračunavani zakoni na 20 °C svih sastava pomoću izračunate vrednosti temperaturske osetljivosti.

Ključne reči: kompozitno raketno gorivo, sagorevanje, stabilnost sagorevanja, cirkonijum karbid.

Стабильность горения смесевых (композиционных) ракетных топлив с использованием карбида циркония

В данной работе представлены исследования влияния циркония с добавками карбида для устойчивого горения смесевых (композиционных) топлив на 12 различных составах на базе гидроксигтерминированного полибутадиена, где некоторые из составов содержали железо (III) оксид как катализатор скорости горения, различных частей твёрдых фаз, долей фракций окислителей и размера частиц перхлората аммония. Измерены и изменения значений вязкости с течением времени в сети и значений предела прочности при растяжении и относительное удлинение при максимальном усилии тестом одноосного растяжения при комнатной температуре, а в том числе и законы скорости горения на двух экстремальных температур, из основе которых рассчитаны законы при 20° С для всех компонентов с использованием расчётных значений температуры чувствительности.

Ключевые слова: смесевое (композиционное) ракетное топливо, сгорание, стабильность горения, карбид циркония.

Stabilité de combustion des propergols composites à zirconium carbure

Dans ce travail on présente la recherche sur les effets du zirconium carbure comme additif pour la combustion stable des propergols composites des 12 différentes compositions basées sur le polybutadiène hydroxyle terminé où certaines compositions contenaient le fer (III) oxyde comme le catalyseur de la vitesse de combustion à différents taux de phases solides, de fractions d'oxydant et de taille des particules d'ammonium perchlorate. On a mesuré les changements des valeurs de la viscosité au cours de durcissement ainsi que les valeurs de la résistance à la tension et de l'extension à la force maximale par le test de la tension uniaxe à la température de chambre. Les lois de la vitesse de combustion à deux températures extrêmes à la base desquelles on a calculé les lois à la 20°C de toutes les compositions données à l'aide de la valeur calculée de la sensibilité de température ont été déterminées aussi.

Mots clés: propergol composite, combustion, stabilité de combustion, zirconium carbure.