PERFORMANCE ENHANCEMENT OF GELLED NITROMETHANE PROPELLANTS USING METALLIC PARTICLES AND HYDRIDS

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Abstract

Nitromethane is a promising candidate to be used as gelled mono-propellant for rocket propulsion. To enhance the performance metallic or other pyrotechnic particles may be added. This study considers the thermodynamic performance of NM mixed with Al, B, Mg, Si, Ti and Zr as well as AlH_3 and MgH_2. The burning behaviour of gelled NM including fumed silica and filled with 10% of these particles was investigated under pressure from 2 to 13 MPa in a window bomb regarding burning velocity and combustion temperature. Stable and self-propagating combustion were found resulting in increased burning velocities and improved ignition behaviour. The replacement of Aluminium and Magnesium by their corresponding hydrides may result in similar specific impulse at lower temperatures. Fumed silica that is widely used as a gelling agent is able to react exothermic with metal filler particles.

Introduction

Liquid propellants for rocket motors show various advantages over solid propellants. They are of high performance, insensitive, and can be externally controlled in thrust or even easily stopped in combustion and later re-ignited [1]. One major disadvantage for defence applications lies in the fact that on impact liquids pour out of the containers endangering the staff and equipment nearby. Jellification of the liquids could overcome this problem [2][3]. In the container the propellant normally behaves like a compact solid when stored or transported. On feeding which induces shear stresses gels become viscous and can be pumped like liquids. Few percents of gelling agent enable the jellification but do not strongly reduce the performance. On sensitivity reasons bi-propellants should be preferred but in many applications monopropellants offer important advantages for a light weight system design by using insensitive liquids.

Nitromethane (CH_3NO_2, NM) is such an energetic, liquid monopropellant with a theoretical specific impulse of $2400\ \mathrm{N\,s\,kg^{-1}}$ [4]-[6]. NM is regarded as a green propellant with low vulnerability and can be produced well-priced and handled easily. It easily can be gelled using fumed silica or organic liquid gelling agent [7]. To increase the fuel specific performance it was successfully proposed to fill NM-gels with moderate amounts of aluminium [8][9]. With respect to ignition and burning behaviour especially under low pressure conditions or in scope of plume signature also other metallic fillers are worth to be investigated according to their influence on performance data and combustion behaviour.

On similar reasons recently metallic hydrides of aluminium and other elements are in the focus of solid propellant investigations [10][11] and also show a high potential for gelled NM.

This study considers the thermodynamic performance of NM mixed with aluminium, boron, magnesium, silicon, titanium and zirconium as well as alane (AlH_3) and magnesium hydride (MgH_2). The burning behaviour of gelled NM filled with these particles was investigated under pressure.

Thermodynamic Performance

Performance calculations were executed with ICT-Code [12] at a constant pressure of 7 MPa expanding to 0.1 MPa for pure nitromethane and NM filled with variable amounts of metals or metal hydrides in steps of 1%. No jelly agents or other additives were considered. Results for mass and volume specific impulse (Isp,m, Isp,V) and adiabatic combustion temperature are presented in Figure 1 to Figure 3.

For filler contents less than 25%, which are realistic for technical applications with acceptable rheological behaviour, aluminium results in specific impulses according to mass and volume with absolute values of 2681 N s kg^{-1} and 3500 N s m^{-3} that would absolutely be acceptable for high performance rocket propellants. For higher metal content the theoretical volumetric specific impulse of zirconium and probably titanium increases to 4770 N s m^{-3} for 70% Zr due to the high molecular weight and the exothermic reactivity with nitrogen that is formed by nitromethane decomposition [13]. But the high molecular weight of these components causes only a minimal influence on mass specific impulse that is usually preferred for most applications. Boron also has no positive effect to specific impulse but anyway may be interesting for ducted rocket applications. For moderate filler ratios of about 10% silicon increases both types of specific impulse. Magnesium also increases mass specific impulse at moderate content. Even this effect is less compared to aluminium. This material is interesting due to its low boiling point and its influence to ignition and burning behaviour and the tendency of forming high melting and very small oxide particles that might be able to reduce plume signature.

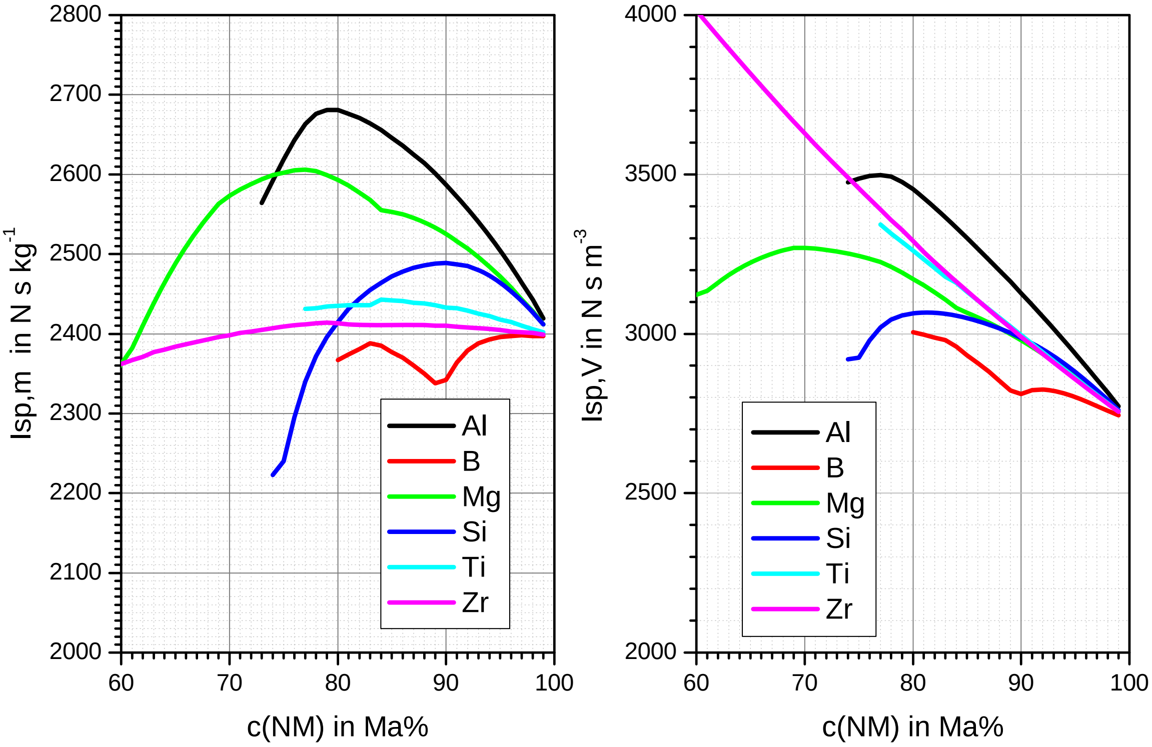


Figure 1 **Mass (left) and volume (right) specific impulse of nitromethane with a number of metallic fillers calculated with ICT-Code (expansion: 7→0.1 MPa).**

The specific impulse of all mixtures correlates widely to the calculated combustion temperatures given in Figure 2. This is very helpful because the combustion temperature is a performance indicator which is much easier to measure in lab-scale tests than specific impulse and will be discussed below.

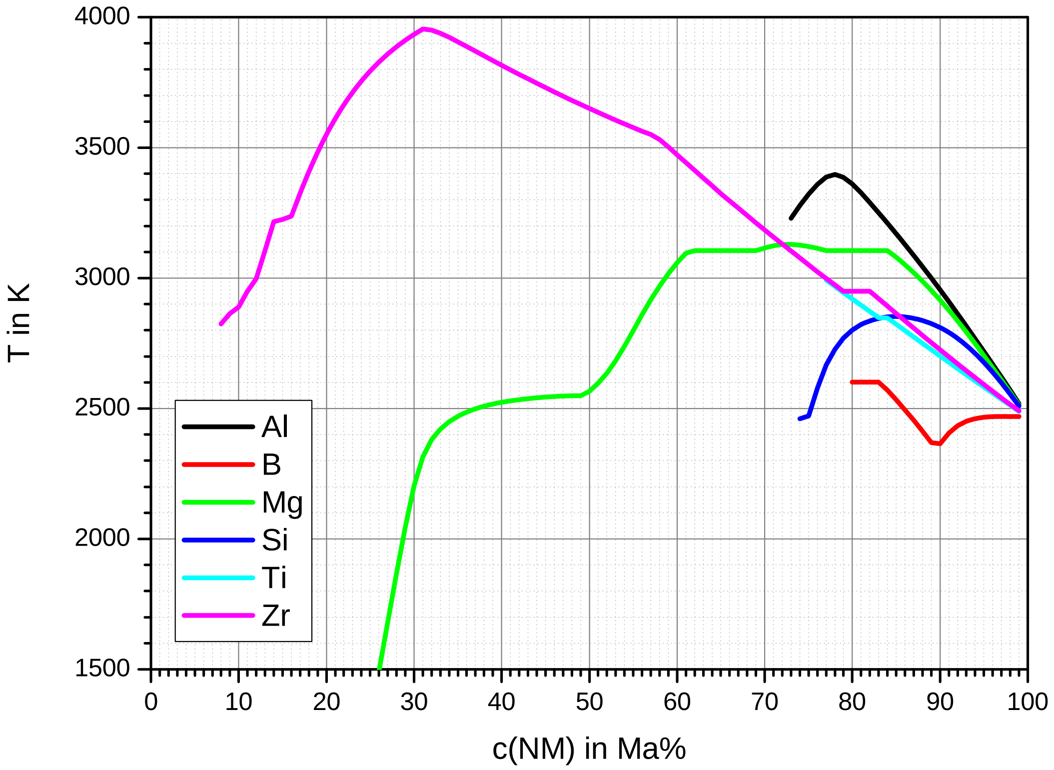


Figure 2 **Adiabatic temperature of nitromethane with a number of metallic fillers calculated with ICT-Code.**

With increasing filler content up to about 20% in all calculations the increasing specific impulse correlates with an obvious shift of water concentration to elementary hydrogen. But also CO_2 concentration decreases in favour of CO. This indicates that at least when considering the chemical thermodynamic equilibrium the filler elements nominally reacts with water and CO_2 according to the reactions:

$H_2O + Me \rightarrow MeO_x + H_2$
$CO_2 + Me \rightarrow MeO_x + CO$

which are strongly exothermic for the cases under consideration.
The low molecular weight of hydrogen enhances the specific impulse. Therefore, due to the formation of elementary hydrogen under combustion conditions with organic rocket propellants, some metal hydrides are recently discussed to substitute pure metal particles with the additional advantage of reducing plume signature. Figure 3 (left) compares mass and volume specific impulse of compositions containing aluminium and magnesium with compositions containing the corresponding hydrides. Generally the effect of hydrides on the specific impulse widely compensates compared to their metallic counterparts at low to moderate filler contents. At 15% to 25%, alane is able to increase mass specific impulse up to 2770 $N\,s\,kg^{-1}$. The main interesting effect of these predictions is that these performance data correlates with up to 500 K lower combustion temperatures that would have a positive impact on the design of the combustion chamber and the nozzle and that have a high potential to reduce plume signature. The later aspect of hydrides is also demonstrated in Figure 4 that compares the main reaction products of the systems NM/Al and NM/AlH_3. Alane not only yields more elementary hydrogen but also reduces the amount of solid aluminium oxide.

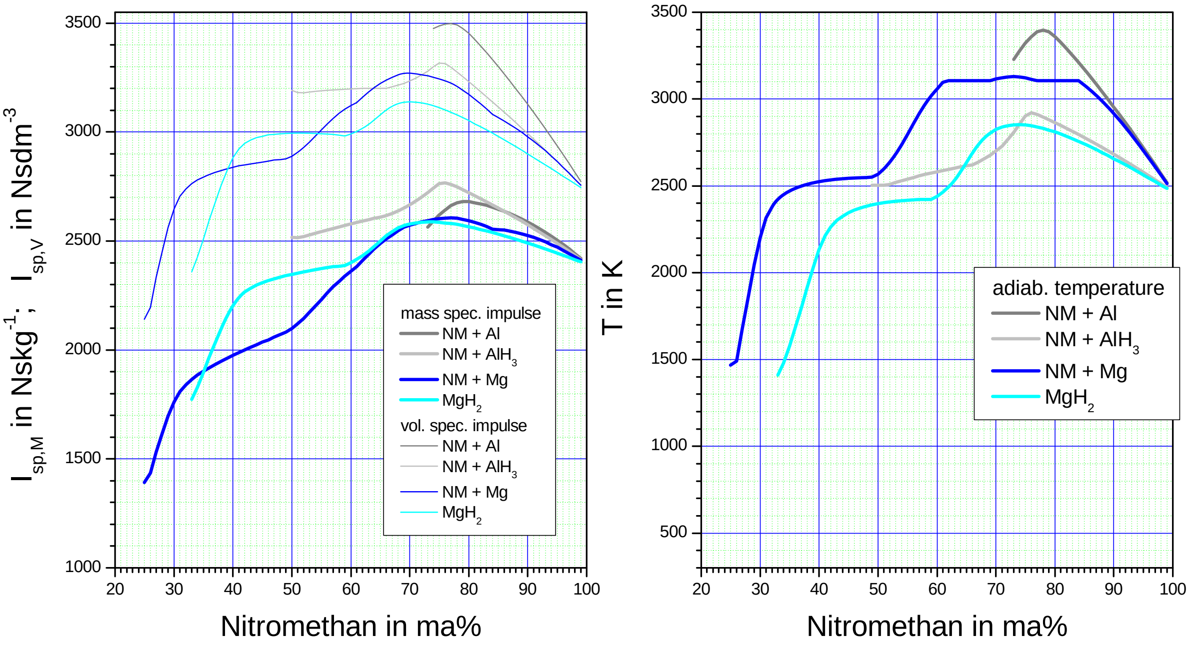


Figure 3 Mass and volume specific impulse (left) and adiabatic combustion temperature (right) of nitromethane with alane and magnesium hydride compared to their elements, calculated with ICT-Code.

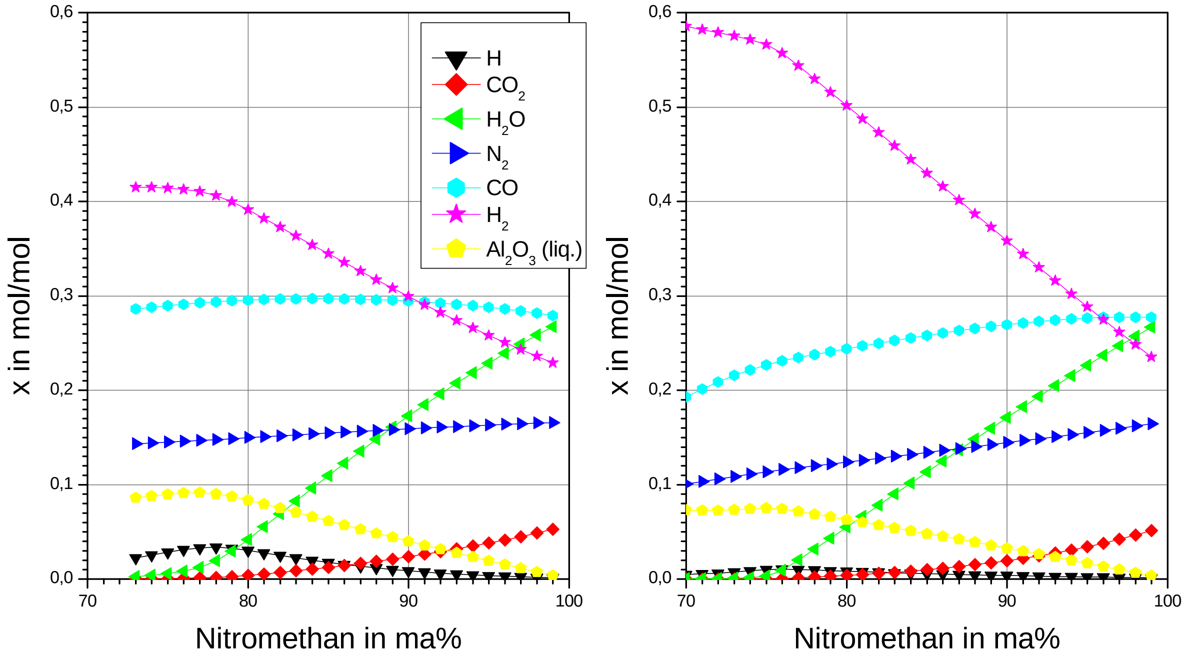


Figure 4 Reaction products of nitromethane with alane and magnesium hydride (right) compared to their elements (left), calculated with ICT-Code

Experimental

Sample Preparation

Propellants consisted of gelled nitromethane filled with 10% of metal or metal hydride particles. Gelling was performed using 5% fumed silica and 5% of an organic gelling agent. As reference pure NM gel was produced. Table 1 summarises the used fillers and their approximate mean particles sizes determined from SEM images.

Filler	Al (Alcan)	Al (Alex)	AlH_3	B (amorph.)	Mg	MgH_2	Si	Ti	Zr
Particle size in µm	5	0.2	20	2	10	30	4	5	6

Table 1 Used filler metals and hydrides and their approximate mean particle diameter

The resulting propellants proved as high viscous and sliceable gels which became a ductile liquid under shear stress conditions. For testing, a sample mass of about 5 g was filled into test tubes using a syringe. Under this shear stress conditions the gels were able to flow. No further rheological investigations were performed. It was specially attended to avoid bubbles inside the tubes filled with gel. The test tubes were made of DURAN glass with an inner diameter of 6 mm and 70 mm in length.

All samples did not show any alteration over a period of about 1 year when stored in a refrigerator. The pure nitromethane sample and the sample with aluminium passed successfully an aging test at 80°C for 26 days.

Set-Up

Pressurised combustion was investigated in a chimney type window bomb equipped with two windows of quartz and crown glass at 1, 2, ... 13 MPa (nitrogen) and at room temperature. The tests were performed in dependence on classical cigarette burning of solid propellants. The test tubes were fixed vertically inside the bomb. For ignition a melting wire was used equipped with a small booster charge of about 0.2 g.

Measurement Equipment

The visible flame front was observed with a digital high-speed video camera (Motion Pro X3) using 100 fps. From the records the flame propagation was achieved using a software code called AVICOR developed at ICT for analysing video files of combustion processes [14][6].

For temperature measurements NIR-spectra were received with a Plane Grating Spectrometer PGS-NIR 2.2 from Carl ZEISS GmbH. The wavelength of this monolithic miniature spectrograph (MMS) ranges from 1 to 2.17 µm. The grating has 300 lines/mm and is blazed for 1.4 µm. This results in a spectral resolution of 16 nm. Integration time varies from 100 µs to 1.6 s with a shortest interval of about 13 ms. As optical entrance a glass fibre is used. Under the applied experimental conditions the field of view was about 10 mm in diameter. This only allowed determining overall temperatures. The evaluation of NIR emission spectra uses the ICT-BaM code to model spectra of gaseous reaction products, soot and continuum radiation. The procedure is described in more detail in [15]. For the recent application the water bands at 1.1 to 1.2 µm, 1.3 to 1.6 µm and 1.7 to 2.1 µm were evaluated. Continuum radiation was regarded as grey-body emission (Planck radiation with constant emissivity).

Results

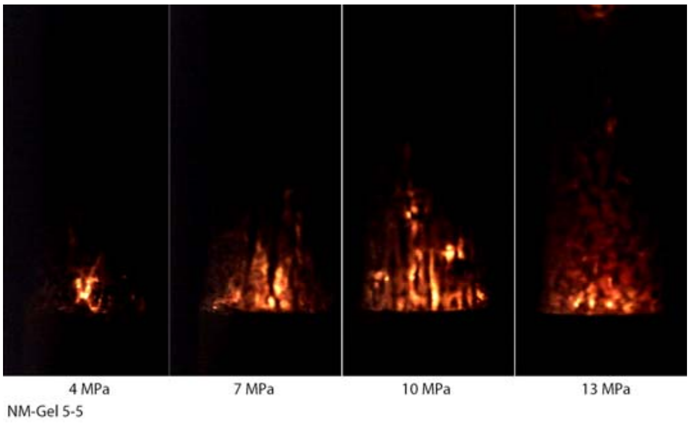
Burning Behaviour

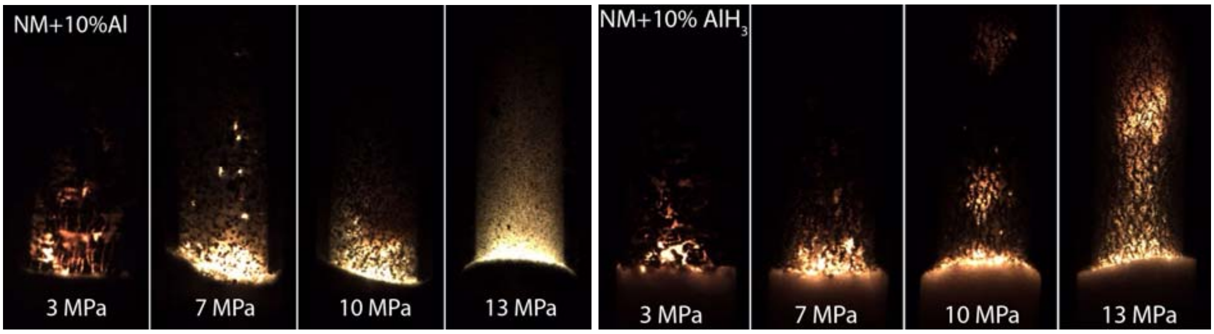
All samples could be ignited above a certain threshold pressure and burned in a widely reproducible manner forming a plain reaction zone orthogonal to the burning direction similar to solid rocket propellants. For most samples this threshold pressure was 0.3 MPa. The sample with MgH_2 also burned at 0.2 MPa. Only the nitromethane reference gel did not burn below 0.4 MPa.

Figure 5 shows screenshots taken from the digital movies at pressures of 3 (4), 7, 10 and 13 MPa. During the combustion process opaque residues were settled at the glass wall affecting the view to the burning zone. The settlements form interesting pattern that are characteristic for the type of propellant and pressure range.

At the burning surface of all samples a glowing dome of condensed material is formed. Its size, shape and structure are also characteristic to the type of propellant. The dome seems to enlarge with increasing pressure, but in most cases this is only because a larger zone is glowing. In many cases these residues remain as a molten stick of frozen slag inside the test tube. For the reference it is clear white and seems to consist of SiO_2-glass from the decomposed fumed silica [7]. For the other samples the slag is dark or coloured and looks similar to frozen metal oxides. So the hypothesis is obvious that this slag contains reaction products of fumed silica and the metallic fillers (see below).

Nevertheless the pictures indicate that the dome of molten slag is either heated over a larger area above the propellant surface by hot reaction gases or might react itself exothermically. At higher pressure the dome of the samples containing alane and magnesium hydride show a second glowing zone in a distance above the surface. The sample containing titanium shows flashing "stars" which are characteristic for the combustion of titanium in different atmospheres [16][17]. The mechanism of formation of these flashes is discussed by the authors elsewhere [18].





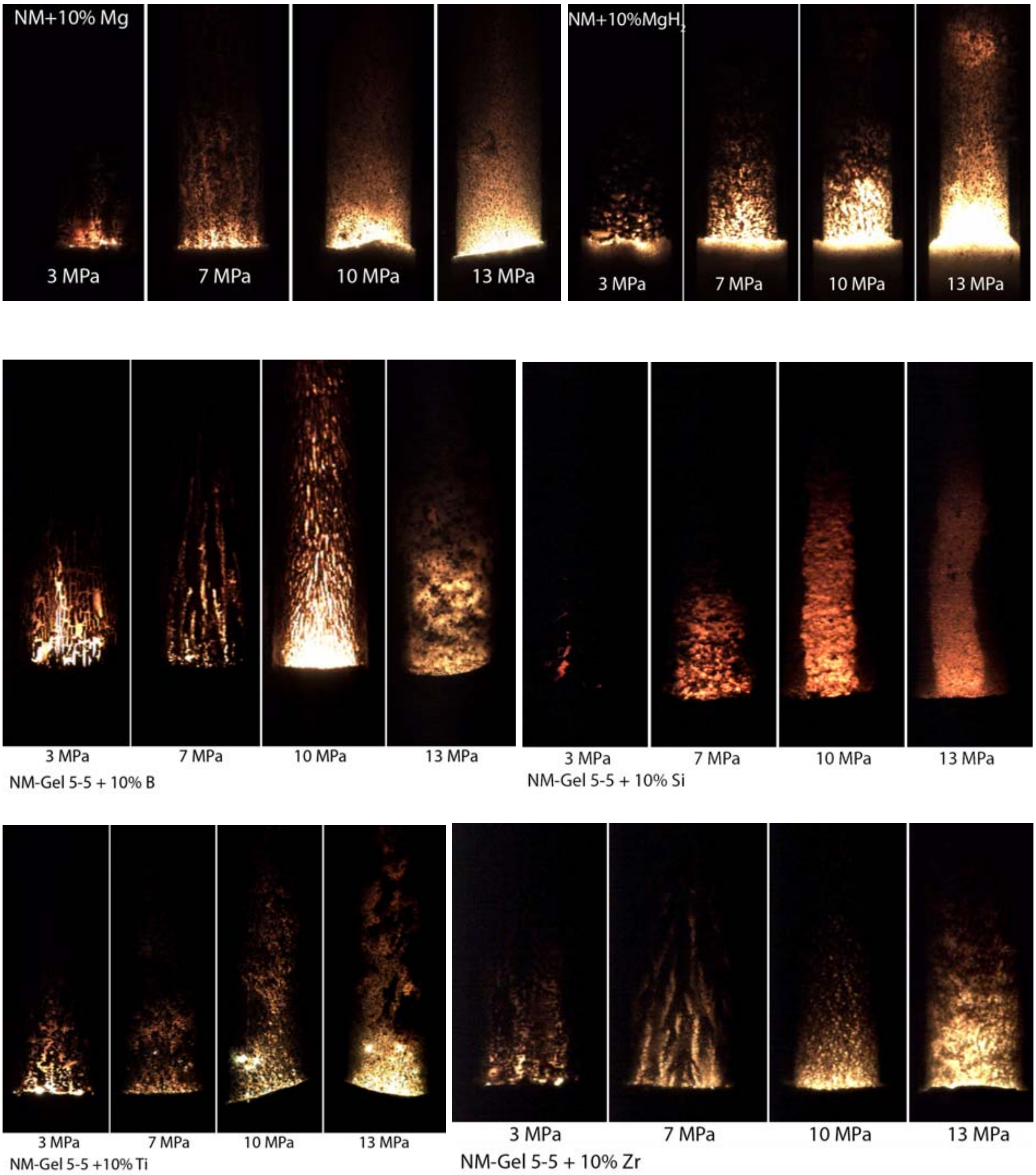


Figure 5 Captured images of burning nitromethane propellants with various fillers at different pressures.

The reaction of all samples results in a linear regression which allows measuring a burning velocity from the slope of regression curves in the same manner like the burning rate of solid propellants [14]. Figure 6 shows examples for samples of gelled NM with 10% magnesium. This behaviour is a very helpful feature of gelled monopropellants for a controlled combustion inside the burning chamber.

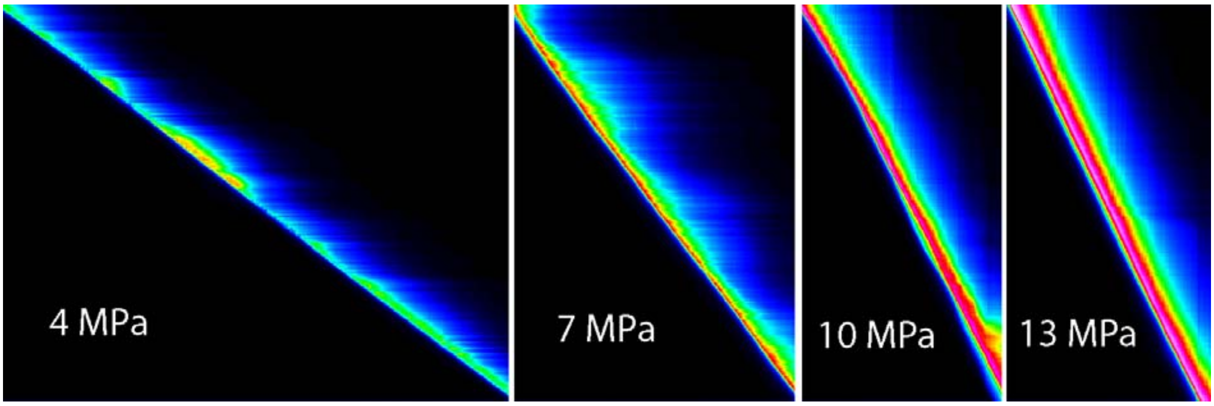


Figure 6 **Regression curves of gelled nitromethane with 10% magnesium**

The resulting burning velocities are shown in Figure 7 and Figure 8 as functions of pressure. Figure 7 summarises the results for the filler particles in comparison to the pure nitromethane gel. Similar to solid propellants the burning velocity of all gelled nitromethane propellants mainly increases with pressure, but does not obey to the power law of Vieille with a constant pressure exponent. Especially in the range from 6 to 9 MPa the burning velocity flattens. In the case of the propellant containing aluminium the curve even shows a kind of mesa-effect with decreasing values with pressure. This agrees well with older investigations [8] [9] realised with mixtures gelled only by using fumed silica. In comparison to them the presented propellants containing an additional fraction of organic gelling agent result in a much smoother and more reproducible burning behaviour.

From Figure 7 it is obvious that silicon has no influence on the burning velocity. But the co-combustion of the other particles increases the burning velocity up to a factor of two and more. The metalized propellants are ignitable at lower pressure. Especially the propellant containing titanium results in an unexpected high burning velocity at 2 MPa.

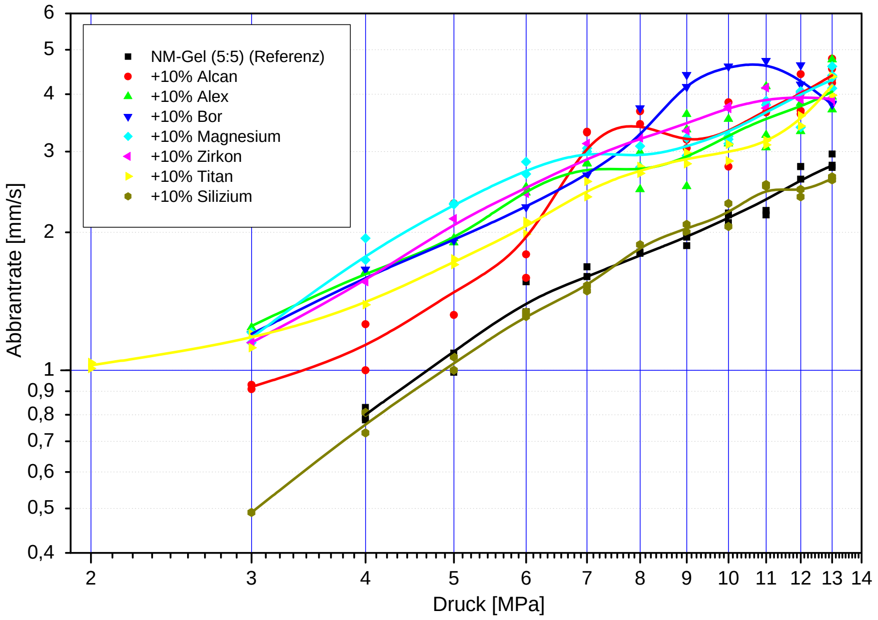


Figure 7 **Burning velocities of gelled nitromethane filled with various 10% of various metal particles.**

Figure 8 compares the burning velocities of the propellants filled with alane und MgH_2 with the ones filled with the respective pure metals and the pure NM-gel. The propellants containing hydrides burn at a similar elevated velocity level than their metallic counterparts. The alane propellant does not show the mesa-effect of Alcan. The propellant containing MgH_2 results in a positive effect on ignitability and burning velocity at pressures below 4 MPa.

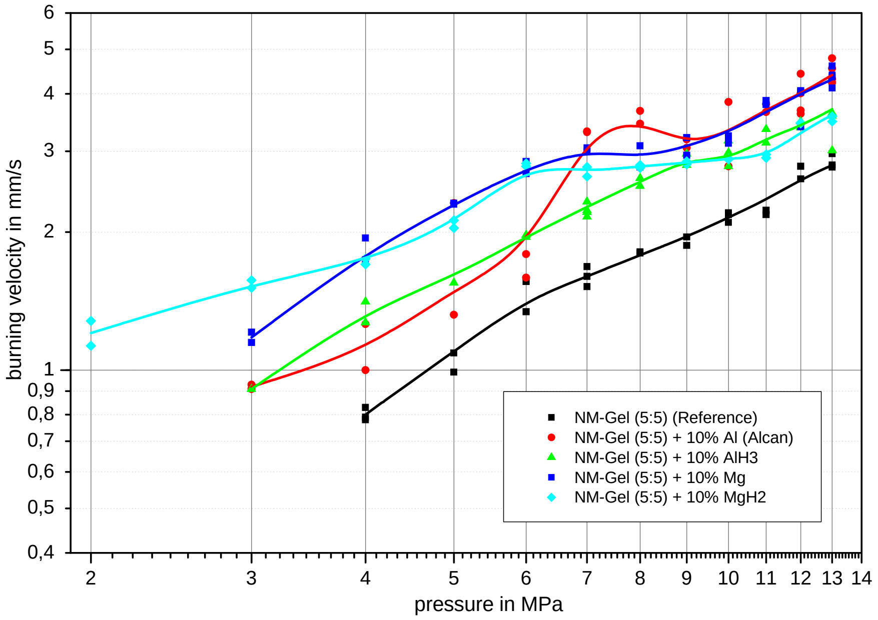


Figure 8 **Burning velocities of gelled nitromethane filled with various 10% of Al, AlH_3, Mg, MgH_3**

The irregularities of pressure dependent burning velocity obviously correspond to the critical point of pure nitromethane at about 6 MPa [19] and 588 K [20]. Also Boyer and Kuo [21] predicted a general influence of this thermodynamic property when the density of vapour is equal to the liquid density. Above this point no evaporation occurs anymore and the heat of evaporation becomes zero. Therefore NM tends first to evaporate before getting decomposed [22]. A correlation of the found pressure dependence of burning velocity and the critical point of nitromethane seams more than supposable and shall be discussed in a future paper.

Temperature

In NIR range, spectral radiation of the particle filled burning NM propellants is dominated by continuum emission overlapped by emitting water bands at 1.4 and 1.8 µm. Compared to the continuum emission the intensity of this water bands is very weak. Only for pure nitromethane gel, water band emission is in a similar quantity than that of the continuum. This continuum radiation is mainly emitted from the intensively emitting dome of slag consisting of condensed material and can be observed in all pictures of Figure 5. It dominates the temperature evaluation using ICT-BaM-Code [15]. Under the chosen experimental conditions it is impossible to determine a temperature from the gas phase. Figure 9 compares the maximum temperatures from the dome of slag for all propellants with filler particles as a function of pressure by assuming grey-body radiation. The fit procedure also took into account the water band emission, but assuming the same temperature as for the continuum radiation. These assumptions resulted in a very good agreement of measured and fitted spectra.

The black curve represents the temperature of the pure NM gel which is neither the coolest nor the hottest one. The temperatures of all propellants increase in a monotone way but not uniformly with pressure. In most cases a jump could be observed in the vicinity of the critical point of nitromethane. The propellant containing silicon shows the lowest combustion temperature. With respect to Figure 7 silicon executes no influence to the burning rate; it may be doubtful if silicon actually takes part in the reaction. The temperature of the propellant containing boron is also lower than the pure NM-gel but this is in good agreement with the ICT-Code predictions in Figure 2. At 7 MPa that was the base of these calculations the propellant containing zirconium has a slightly lower temperature than the NM reference that is in contrast to Figure 2 and indicates that this material does not react like predicted. At least at 7 MPa the propellants containing aluminium, magnesium and titanium feature temperatures that are several hundred Kelvin higher than the NM-reference, which is in good agreement to the thermodynamic predictions.

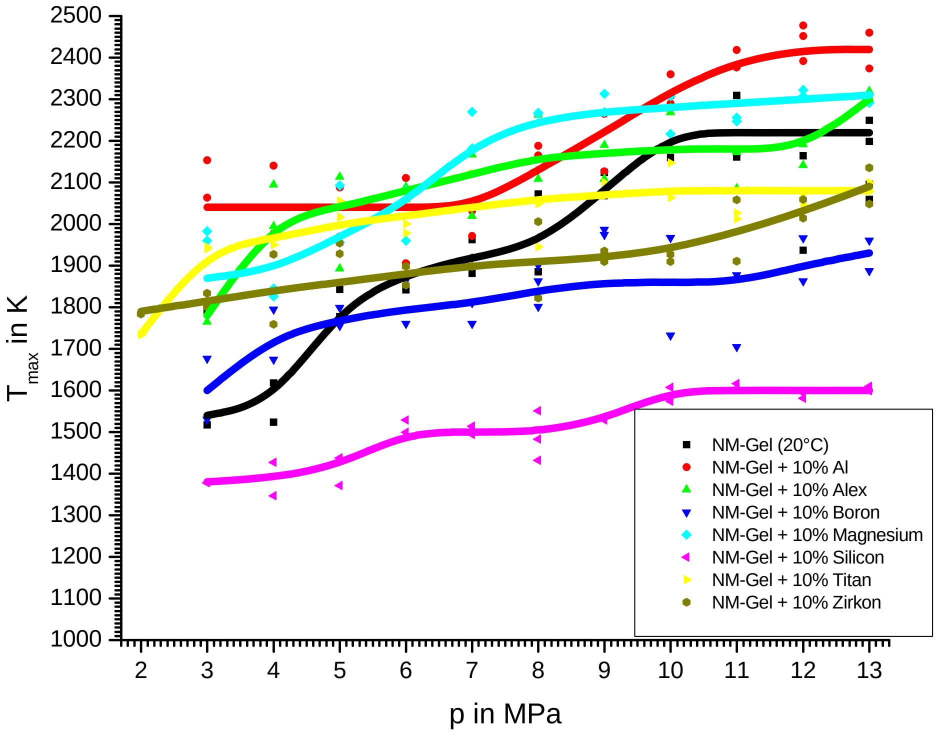


Figure 9 **Temperature of continuum emission in NIR from the gelled nitromethane filled with various 10% of various metal particles.**

Figure 10 compares the temperatures of gelled nitromethane filled with Aluminium (left) and Magnesium (right) and the corresponding hydrides also determined from continuum of the dome of slag. The vertical lines indicate the received temperature intervals during the total reaction, the bold lines show trend of the respective mean values. In most cases the mean temperature of the hydrides are 100 to 200 K lower than their corresponding metal fillers. This is at least in a qualitative agreement to the thermodynamic predictions in Figure 2. Only below 6 MPa the composition of NM/MgH_2 is hotter than NM/Mg.

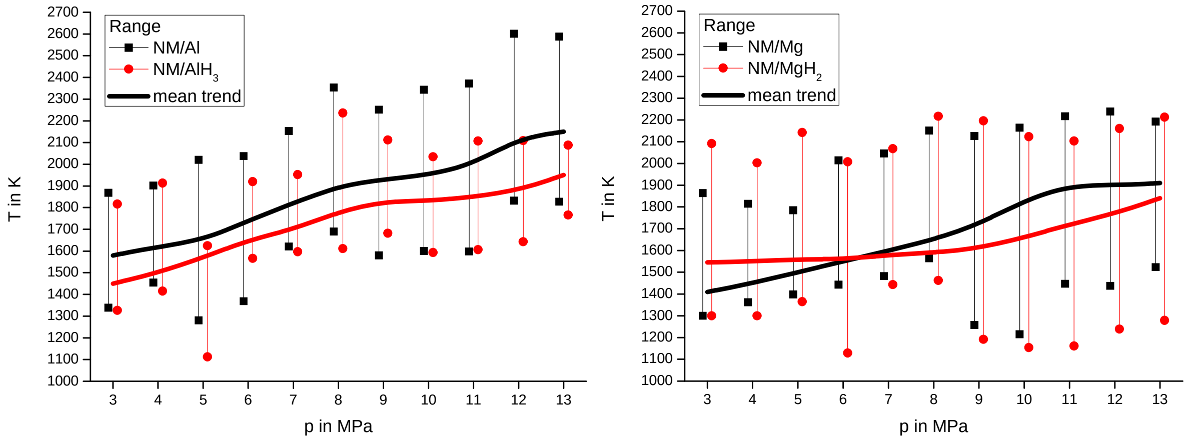


Figure 10 **Temperature of gelled nitromethane filled with metal and corresponding hydride; Al/AlH_3 (left), Mg/MgH_2 (right)**

Thermite Reaction with fumed Silicon

During the reported investigations the question arises if there could be a reaction between the particles and the fumed silica maybe according to a thermite type reaction:

$SiO_2 + 4/3\ Al \rightarrow 2/3\ Al_2O_3 + Si$ $\Delta_R H=-209$ kJ/mol
$SiO_2 + 2\ Mg \rightarrow 2\ MgO + Si$ $\Delta_R H=-294$ kJ/mol

In this case fumed silica would not act like an inert and energy absorbing material but could be reduced exothermically. This reaction was not considered by the ICT-Code calculations in Figure 2 and could also contribute to understand the above mentioned discrepancy to the measured results. Figure 11 presents thermodynamic equilibrium calculations performed with EKVI-Code that emphasize this assumption [23]. The proof of this assumption was difficult to derivate from the above mentioned residues that were found as frozen slag with mainly amorphous structure not able to be analyzed using X-ray diffraction. To verify that fumed silica is able to react with aluminum and magnesium stoichiometric mixtures were produced, filled in the same test tubes than the investigated gels and ignited in the window bomb under nitrogen. The experiments result in successful ignition developing progression velocities of several centimeters per second. Maximum reaction temperatures of 1900 K (Al + fumed silica) and 2000 K (Mg + fumed silica) were measured.

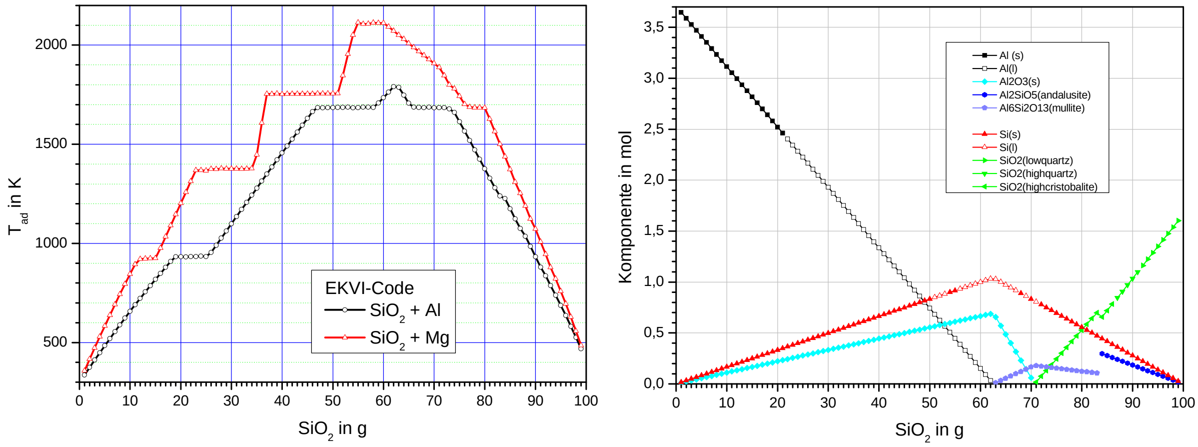


Figure 11 **Thermodynamic equilibriums calculations of aluminium and magnesium with silica; adiabatic temperature (left); reaction products of Al and SiO_2 (right).**

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