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REVIEW PAPER

Recent developments in ceramic microthrusters and the potential applications with green propellants: a review

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Abstract

Conventional chemical propellants such as hydrazine and ammonium perchlorate have been used within the realm of contemporary space propulsion devices and are well established owing to their rich heritage. However, their limitations such as toxicity, difficulty in operational handling and environmental impacts have raised concerns. In view of these limitations, the significance of green propellants such as hydroxylammonium nitrate, hydrogen peroxide (H_2O_2) and ammonium dinitramide has become more pronounced. In this paper, recent developments in ceramic microthrusters and the associated ceramic microfabrication techniques are reviewed. The characteristics of green propellants are examined, followed by the evaluation of previous attempts to incorporate green propellants into ceramic microthrusters. This has further unveiled the possibilities of green and clean space missions in the future.

Keywords Green propulsion · Ceramics · Microthrusters · Hydroxylammonium nitrate (HAN) · Ammonium dinitramide (ADN) · Hydrogen peroxide (H_2O_2)

Introduction

Microelectromechanical system (MEMS) has initiated the miniaturization of conventional propulsion system by reducing system mass and volume significantly. Three motivations behind the miniaturization and development of micro-spacecraft are to (Rossi et al. 2001; Zhang et al. 2004):

I. reduce mission cost and increase launch rates by reducing launch mass;
II. reduce mission risk and increase mission flexibility [launching clusters of micro-spacecraft rather than a large conventional spacecraft];
III. discover new application areas of space technology.

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In micropropulsion systems, the term "micro" can refer to either of two things: (1) a propulsion system which delivers thrust in the order of micro-newton (μN) or (2) a propulsion system which is in the micrometer (μm) scale (Lekholm et al. 2013). The former does not have requirements on maximum size or mass and the latter can be designed to produce different levels of thrust. Small satellites, in particular nanosatellites (< 10 kg), require miniaturized propulsion system of low thrust, small system mass and compact designs. The advent of microelectromechanical systems (MEMS) has introduced a new market with incredibly small-scale designs.

A review of chemical micropropulsion and various microthruster fabrication technologies used in micro-spacecraft has been carried out previously (Wu et al. 2014). Although the development of micropropulsion systems through silicon MEMS technology has been considerably well established, it is not free from limitations. Their efficiency is low due to the high thermal conductivity of silicon which was originally developed and most commonly used in microelectronic industries (Cheah and Low 2015). Initiative was taken to improve the thermal insulation of the system by reducing the contact area with the combustion area. However, it resulted in more complex fabrication steps (London et al. 2001). Owing to this disadvantage, ceramic materials were explored for use in micropropulsion devices. This is due to the better thermal insulation of ceramic materials, which can improve the performance of the system over silicon-based systems. The other advantages of ceramic materials are their high mechanical strength in the fired state with multilayer structures (where few ceramic sheets are printed and stacked on top of the previous layer, laminated and sintered together), ability to withstand harsh environment created by high temperatures and good sealing capabilities which makes it an excellent choice for devices (Yuan and Li 2009; Lekholm et al. 2013; Huh and Kwon 2014). For example, Yetter et al. (2003) built an alumina microthruster and demonstrated the combustion of hydrogen/air at a chamber pressure of approximately 8 atm, Miesse et al. (2005) developed a mesoscale alumina burner to study the flame dynamics of gas combustion, while Jiang et al. (2015) fabricated ceramic-based mesoscale fuel processor for onboard production of syngas fuel. Table 1 summarizes the properties of common materials used to develop micropropulsion devices.

Among the chemical propellants, solid propellant of hydroxyl-terminated polybutadiene–ammonium perchlorate (HTPB/AP) (Zhang et al. 2004; Thakur et al. 2010) and liquid monopropellant of hydrazine (Yuan and Li 2009; Kundu et al. 2010; Gauer et al. 2013) are commonly used in various micropropulsion devices. Although these propellants have been well established owing to the rich heritage from previous missions, their limitations of toxicity, difficulty in operational handling and environmental impacts have raised concerns. For example, toxicity and flammability of hydrazine require special ground handling procedures which would incur higher cost (Marshall and Deans 2013). Ammonium perchlorate was reported to form a vast amount of hydrochloric acid upon combustion. Space shuttle and Ariane 5 generated 580 and 270 tons of concentrated hydrochloric acid, respectively, per launch (Wingborg et al. 2008). In view of these limitations, green chemical propellants such as hydroxylammonium nitrate (Kuwahara et al. 1997; Courthéoux et al. 2006; Meng et al. 2009; Amrousse et al. 2017), hydrogen peroxide (Hitt et al. 2001; Plumlee et al. 2007; Kuan et al. 2007; Kundu et al. 2013; Huh and Kwon 2014) and ammonium dinitramide (Larsson and Wingborg 2011; Pang et al. 2013) have emerged as promising alternatives to the conventional chemical propellants.

In-space propulsion concepts can be broadly categorized into electric and chemical propulsions, depending on the source of power extraction. This review focuses primarily on the chemical micropropulsion systems developed using ceramics as structural material. Although cold gas and vaporizing liquid propulsion concepts belong to neither electric nor chemical propulsion, they are included in this review due to their simplicity which is ideal for proof-of-concept studies. This is followed by the review on characteristics of various green propellants and previous attempts to incorporate them, in particular hydrogen peroxide, into ceramic-based micropropulsion systems. Figure 1 summarizes the topics which will be covered in this review paper.

Table 1 Properties of materials used for developing micropropulsion devices

	Silicon[a]	99.7%[b] alumina	Zirconia[b] (3Y-TZP)
Compressive strength (MPa)	120	2100	2000
Fracture toughness (MPa $m^{1/2}$)	3–6	4	10
Modulus of elasticity (GPa)	112	330	205
Maximum service temperature[c] (°C)	1350	1840	1700
Thermal conductivity (W/m K)	125	29	2
Corrosion resistance	x	✓	✓
Design flexibility	✓	✓	✓

[a]The properties of silicon were extracted from Ferro-Ceramic Grinding Inc.'s material data sheet

[b]The properties of alumina and zirconia were extracted from Dynamic-Ceramic Ltd's material data sheet

[c]Temperature at which the sample remains structurally intact

Fabrication technologies for ceramic microthrusters

Cold gas, solid or liquid monopropellant, bipropellant and vaporizing liquid are examples of ceramic microthrusters that have been reported in open literature. Vaporizing liquid microthruster (VLM) can be used multiple times, depending on the quality of the valve and volume of fuel storage, but it consumes more electric energy to vaporize the liquid propellant (Cheah and Low 2015). Cold gas microthrusters have low complexity of their subsystems and are well suited for mass-critical applications (Lekholm et al. 2013; Köhler et al. 2002; Ranjan et al. 2018). However, there are risks of leakage of the highly pressurized gas during long missions which can be fatal. On the other hand, monopropellant microthruster is a promising alternative in comparison to bipropellant

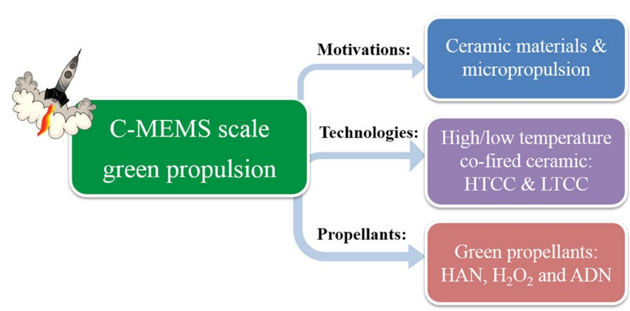

Fig. 1 Graphical illustration of the topics discussed in this review

microthruster for attitude control. It is inherently less complex in terms of design, as the mixing of fuel and oxidizer is not required (Plumlee et al. 2007; Khaji et al. 2017).

In co-fired ceramic devices, each layer can be processed differently and assembled to form a final structure. In this route, ceramic green tapes are first prepared by conventional tape casting technique (Wu and Lin 2010). They are then patterned on the green tapes using laser machining, micro-milling or micro-punching. Integration of heating elements or conductive paths into the micro-systems is carried out via screen printing of conductive paste on tapes. Finally, the green tapes are laminated and co-fired at a high temperature to form ceramic micro-components including microthruster. The two common technologies for ceramic MEMS microthrusters are low-temperature co-fired ceramics (LTCC) and high-temperature co-fired ceramics (HTCC). The firing temperature of LTCC is lower than that of HTCC due to the presence of high content glass phase in LTCC (Induja et al. 2015). In addition to co-fired ceramic technologies, stereolithography and hot embossing are two potential fabrication techniques of ceramic microthrusters.

Low-temperature co-fired ceramics (LTCC)

The firing temperature for LTCC is below 1000 °C (Sakamoto et al. 2017). The LTCC technology which requires no expensive equipment and complicated fabrication steps was first adapted to develop monopropellant (Zhang et al. 2004; Plumlee et al. 2007; Wu and Yetter 2009; Cheah and Chin 2013) and bipropellant microthrusters (London et al. 2001; Wu and Lin 2010). The better thermal insulation of LTCC tapes has improved the performance of the systems over silicon-based systems as reported by Zhang et al. (2004). Also, Plumlee et al. (2007) investigated the decomposition temperature and heat transfer effects in a catalyst chamber of LTCC hydrogen peroxide thrusters. The authors concluded that the low thermal conductivity of LTCCs make them suitable fabrication materials to produce reliable micropropulsion systems. The feasibility of using LTCC tape technology to fabricate a microscale counterflow diffusion flame burner with integrated optical sapphire windows was demonstrated (Wu and Yetter 2008). The group of authors was also successful in embedding spark electrodes and ion probes in a ceramic mirothruster using the LTCC tape technology (Wu and Lu 2012). The embedded ion probes provided signal traces assisting characterizing reaction propagation velocities, where a velocity above 2000 ms^{-1} was achieved prior the channel exit.

However, since the maximum servicing temperature of LTCC tapes is limited to 900 °C, HTCC technology has been adapted for the development of high-performance micropropulsion systems that operate at higher temperatures (Zhang et al. 2005). Figure 2 shows the process flow diagram for fabricating an LTCC microthruster. Although the process of LTCC is similar to that of HTCC, LTCC is more cost-effective as it uses low resistivity conductors such as silver, gold, copper and alloys with palladium and platinum, due to the relatively low firing temperature of LTCC of approximately 900 °C (close to the melting points of gold and silver).

High-temperature co-fired ceramics (HTCC)

Zirconia and alumina are the two common materials for fabrication of HTCC microdevices. The firing temperature for HTCC ceramics is around 1600 °C and, unlike LTCC, no glass material is used as the binding phase (Zhang et al. 2005). HTCCs are widely recognized for their superior thermal–mechanical properties such as good mechanical strength, high fracture toughness and low thermal conductivity. Besides, exceptional thermal shock resistance of zirconia makes it appealing for developing chemical micropropulsion systems. Since the firing temperature of HTCC is at 1600 °C, it only allows co-firing of conductors such as platinum and tungsten. The HTCC-based micropropulsion system was first demonstrated in cold gas and vaporizing liquid concepts (Sun et al. 2012; Lekholm et al. 2013; Cheah and Low 2015) as they are among the simplest propulsion concepts. Cheah and Low (2015) fabricated a vaporizing liquid microthruster (VLM) via HTCC technology using zirconia as the structural material (Fig. 3).

Stereolithography

Stereolithography is an additive manufacturing technique that uses ultraviolet (UV) laser across the surface of photo-curable vat of liquid resin during the building

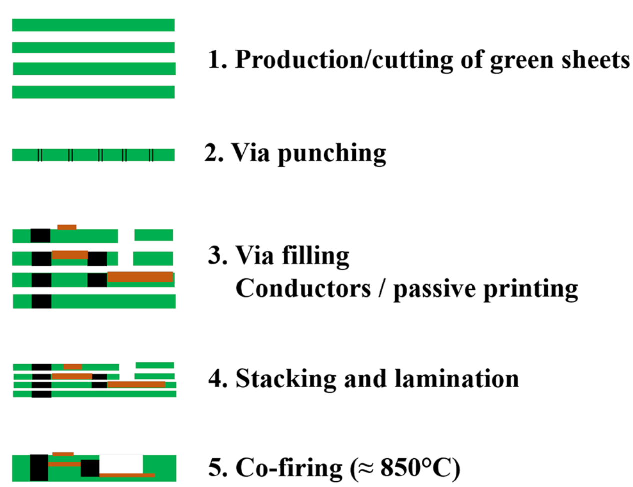

Fig. 2 General fabrication process flow of LTCC microthrusters where layers are processed in parallel, stacked, laminated and co-fired

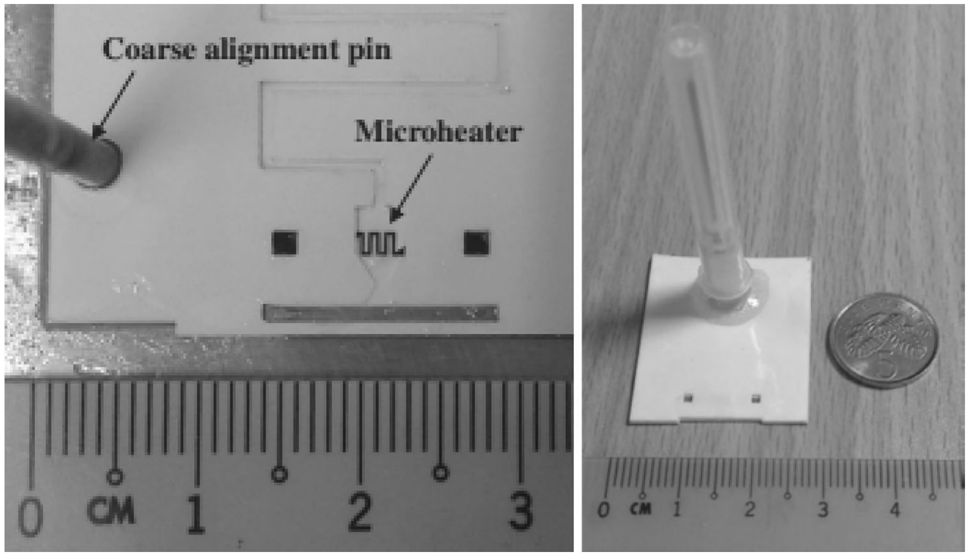

Fig. 3 Vaporizing liquid HTCC microthruster in comparison to a Singaporean 5 cent coin (Cheah and Low 2015)

up of each layer, where exposure to UV light cures and solidifies the traced pattern. The solidified layer will be moved down by a single layer thickness inside the liquid bath such that the resin-filled blade sweeps across the previously cured layer and the process is repeated to trace the subsequent layers adhering to the previous layers. Zhang et al. (1999) filled the UV curable polymers with 33 vol% Al_2O_3 with a diameter size of 200 nm. A green body was successfully fabricated with lateral resolution up to 2 µm with the aid of focusing optics and 15 µm-thick single layers on a substrate. The fabricated ceramic structures were sintered at 1400 °C and exhibited low shrinkage. In another study, Provin and Monneret (2002) fabricated smooth 3D structures in micrometer range via a similar scheme of process. UV light was projected from an Hg lamp using an LCD screen which has a VGA resolution of 640 × 480 pixels to define single layer patterns in the exposure steps. The authors reported that solid loading of 24 vol% alumina assisted in achieving a depth resolution of < 10 µm.

Ceramic microthrusters using stereolithography technique was first reported in a work by Yetter et al. (2003), where an alumina microthruster with contoured axis-symmetric nozzle was fabricated. The resin was a highly concentrated colloidal dispersion of alumina powder in an aqueous solution of ultraviolet curable polymers. The ceramic green body obtained from the process was later sintered to full density. The authors reported stable combustion of hydrogen–air mixture at a chamber pressure of 8 atm and the ability of the thrusters to survive repetitive start-ups, shutdowns and continuous operation at high gas temperatures (> 1727 °C) (Table 2).

Green propellants

The desirable characteristics for any propellant are high specific impulse, reproducible burning rate and ignition characteristics, ease of manufacturing, low cost and good aging characteristics. From the safety point of view, propellants should produce little smoke, not be prone to combustion instability and be safe for the intended range of operation and storage. Table 3 compares the performance parameters, i.e., specific impulse and density impulse of HAN, H_2O_2, ADN and hydrazine.

For HAN, H_2O_2 and hydrazine, specific impulse values are provided at a chamber pressure of 69 bar and nozzle expansion ratio of 100 under vacuum conditions. For ADN (LMP 103 s), these values are provided at a propellant feed pressure between 5.5 and 22 bar with conical nozzle expansion ratio of 50:1. Although hydrazine exhibits the best specific impulse value in comparison to HAN and H_2O_2, the toxicity and carcinogenicity of hydrazine raise concerns within the research community. Besides, Kuo (2010) have reported that a comparable specific impulse of HAN with hydrazine can be attained when the operating temperature of HAN is increased by adjusting the composition of the HAN mixture. Besides, operational lifetime of the catalyst would be shorter when composition of HAN based propellant is highly energetic. The following sections will discuss three well-known green propellants: HAN, H_2O_2 and ADN.

Hydroxylammonium nitrate (HAN)

Hydroxylammonium nitrate (HAN, $NH_3OH^+NO_3^-$) has emerged as a promising choice of "green" propellant. HAN is an oxygen-rich component which dissolves in water as an

Table 2 Performance of selected thrusters fabricated from LTCC, HTCC and silicon

Material	Type	Power	Peak thrust (mN)	Impulse or specific impulse	References
LTCC (alumina–glass)	Monopropellant	1350 W[a]	197,197	0.003 N s	Wu and Yetter (2009)
	VLM	9.2 W	0.068	6.9 s	Karthikeyan et al. (2012)
	Solid	1.33 W	446	31.55 s	Zhang et al. (2005)
	Solid	N/A	19.5	N/A	Thakur et al. (2010)
	Bipropellant	N/A	1.970	N/A	Wu and Lin (2010)
HTCC (zirconia)	VLM	4.0 W	0.634	31 s	Cheah and Low (2015)
	Monopropellant	N/A	0.96	106 s	Khaji et al. (2017)
	Cold gas	2 W	–	71 s	Lekholm et al. (2013)
Silicon	Solid	0.08 W	3.5	N/A	Chaalane et al. (2015)
	Solid	N/A	674	333 s	Churaman et al. (2015)
	VLM	2.0 W	0.12	N/A	Maurya et al. (2005)

[a]Calculated using DC voltage input of 45 V and clipping current set at 30 A

Table 3 Specific and density impulse of various propellants

Propellant	Vacuum specific impulse (N s/kg)	Vacuum density impulse (N s/m^3)	References
HAN	1961	2.629×10^6	Wernimont (2006)
H_2O_2	1883	2.541×10^6	Wernimont (2006)
ADN	2310	2.724×10^6	Anflo et al. (2009b)
Hydrazine	2402	2.268×10^6	Wernimont (2006)

ionic solution. Due to its low toxicity level, HAN requires no special ground handling and is suitable for long-term storage. In comparison to other common energetic materials, decomposition of HAN is more complex, where it occurs in stages owing to its multicomponent property. For example, Koh et al. (2013) described the combustion of HAN as a three-stage reaction of (1) initiation, (2) ignition and (3) combustion. A similar trend of three-stage combustion mechanism was also initially proposed by Oxley and Brower (1988).

Thermal and catalytic techniques are commonly used in macro-scale propulsion systems. These techniques require the preheating process which can lead to enhanced heat loss due to the increased surface to volume ratio in the micro-scale system. To address this deficiency, Yetter et al. (2003) developed a new ignition technique with electrolysis where direct current (DC) was applied directly to the propellant to initiate decomposition through non-spontaneous redox reaction. The authors concluded that the overall combustion process of HAN was more efficient with reduced heat loss. Other advantages of the electrolytic decomposition mechanism are that it can be initiated at room temperature, requires reduced power and has enhanced system reliability. The reaction starts with electrolysis of water:

At the anode:

$$H_2O \rightarrow {}^1\!/_2 O_2 + 2H^+ + 2e^-. \quad (1)$$

Production of protons from electrolysis of water develops the reaction below:

$$NH_3OH^+NO_3^- + H^+ \rightarrow NH_3OH^+ + HNO_3. \quad (2)$$

At the cathode:

$$2NH_3OH^+ + 2e^- \rightarrow 2NH_2OH + H_2. \quad (3)$$

Thus, from (1), (2) and (3), the overall electrochemical reaction is as follows:

$$2NH_3OH^+NO_3^- + H_2O \rightarrow 2NH_2OH + 2HNO_3 + H_2 + {}^1\!/_2 O_2. \quad (4)$$

Ionized HAN undergoes a series of thermal decomposition steps where water content is vaporized into the HAN solution. This is followed by the explosion period as nitric acid reacts with hydroxylamine to produce intermediate gas species (NO_2, NO and HNO_3) and a later decay period to form decomposition gases (N_2, O_2 and H_2O). The overall reaction for complete HAN decomposition is as follows (Yetter et al. 2003; Meng et al. 2009):

$$NH_3OH^+NO_3^- \rightarrow N_2 + O_2 + 2H_2O + \text{heat}. \quad (5)$$

Meng et al. (2009) have reported that via the electrolysis process, the HAN decomposes to form additional hydrogen and oxygen gases which enhance the ignition and combustion processes. As shown in (5), the complete decomposition of HAN releases only water vapor, nitrogen and oxygen gas which can be considered as "green" propellant with minimum impacts to the environment. In 2008, Wu et al. (2008) developed a ceramic microthruster using LTCC tape technology and tested its performance using HAN-based liquid monopropellant. The authors reported successful ignition of microthruster where a thrust output of ≈ 200 mN was recorded with a voltage input of 45 V. Although ignition delay was only 224.5 ms, cracking of the thruster body was observed when ignition was rapid. In another study, Cheah and Chin (2011) fabricated an Al_2O_3–SiO_2 ceramic microthruster which consists of propellant reservoir, injector, electrodes, combustion chamber and micronozzle, all integrated into a single volume of 20 mm × 20 mm × 5 mm. The performance of the ceramic microthruster (with 15° and 30° linear micronozzle) was numerically predicted using FLUENT simulation software with 85% HAN binary solution as propellant. The authors reported that 15° linear micronozzle with longer expander section develops thicker viscous layers which degrades performance, while 30° displays higher thrust efficiency and specific impulse.

Although HAN is a good alternative as chemical propellant, its combustion temperature is relatively high. Furthermore, catalytic decomposition and ignition of HAN require preheating of the catalyst bed. This poses challenges to the structural material of the thruster body.

Hydrogen peroxide (H_2O_2)

Hydrogen peroxide has been used as rocket monopropellant and an almost non-volatile oxidizer since the 1940s. This propellant offers the aerospace community an excellent approach of using an environmentally friendly propellant with greatly reduced toxicity and low storage and handling costs. Besides, studies have reported that propulsion-grade hydrogen peroxide has a remarkable history of long-term safe production and use in power and propulsive devices (Rarata et al. 2016; Florczuk and Rarata 2017).

The best performances can be obtained by using the highest concentration, i.e., 100% hydrogen peroxide. Nonetheless, owing to the compromise between production cost and obtained performance, 98% HTP (high test peroxide) is the typical concentration in various rocket applications. Furthermore, studies have reported that new propellants coupled with 98% HTP deliver higher thrust for a given volume of propellant than hydrazine derivate in contact with nitrogen tetroxide (Kang et al. 2017). In most cases, the mechanism for propulsion occurs from catalyzed chemical decomposition of hydrogen peroxide. Examples of catalysts include silver, platinum, iridium and manganese oxides (MnOx). The catalysts are used as they can dramatically increase the reaction speed during decomposition of hydrogen peroxide, since non-catalyzed reaction is quite slow and unsuitable for thruster application. The reaction governing the decomposition of hydrogen peroxide is as follows:

$$2H_2O_2 \rightarrow 2H_2O + O_2 + \text{heat}. \quad (6)$$

Based on the reaction products, hydrogen peroxide can be considered as "green" propellant since its complete decomposition only releases water vapor, oxygen gas and heat with minimal impacts to the environment. Khaji et al. (2016) developed an alumina microthruster with an integrated heater, catalytic bed with platinum paste and two temperature sensors. The thruster was tested using 30 wt% hydrogen peroxide at a flow rate of 50 µl/min and complete decomposition was observed above 3.7 W where the catalytic bed reached a maximum temperature of 147 °C. The thruster was successfully operated to 307 °C at which point it cracked (Fig. 4). In contrast, Rusek (2004) have shown that a higher concentration of hydrogen peroxide (90%) is able to generate a temperature of 740 °C during decomposition when exposed to silver catalyst.

Khaji et al. (2017) fabricated and tested alumina microthruster with 31 wt% hydrogen peroxide. They reported that the small reaction chambers showed 1.5 times higher dry temperature tolerance in comparison to devices with 4.2 times larger chambers (in terms of volume). It was also found that bigger devices consumed 2.9 times more power than devices that are 8.6 times smaller (in terms of chip size). Assuming complete decomposition of hydrogen peroxide, thrust and specific impulse of 0.96 mN and 106 s were calculated. In case of extreme evaporation where there was no propellant decomposition, lower thrust and specific impulse of 0.84 mN and 92 s were achieved, respectively.

Ammonium dinitramide

In early years, ammonium nitrate (AN) was considered as an environmentally friendly alternative to the commonly used ammonium perchlorate (AP). However, its use was

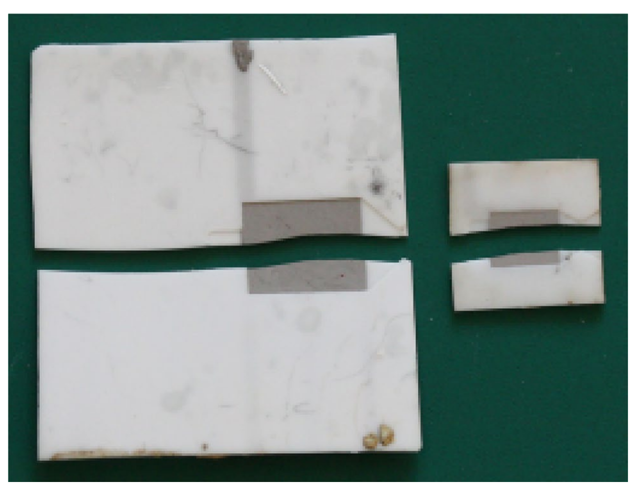

Fig. 4 Microthruster cracked in two halves along the catalytic chamber (Khaji et al. 2017)

precluded due to poor performance. In later studies, ammonium salt of dinitramide acid $NH_4N(NO_2)_2$, known as ammonium dinitramide was envisaged in replacing AN. ADN was originally synthesized by the Soviet Union in 1971 and has attracted wide interest as a potentially useful energetic oxidizer for rocket propellants owing to its clean and environmentally friendly exhaust products upon combustion (Rossi et al. 1992). Many studies have reported ADN as a green propellant since it eliminates the emission of chlorinated exhaust products, produces less smoke and exhibits higher specific impulse (Östmark et al. 2000; Klapötke et al. 2008; Zhang et al. 2014).

Various studies on ADN such as ignition characteristics, safety, stability and purity have been reported to date (Wingborg et al. 2004; Jones et al. 2005; Anflo et al. 2009a; Larsson and Wingborg 2011). The preferred monopropellants are generally stabilized compositions of ADN–water–glycerol or ADN–water–methanol. In 2005, Wingborg et al. (2005) demonstrated that ADN-based FLP-105 has 60 and 10% improvement in density impulse and specific impulse, respectively, in comparison to hydrazine. Another ADN blend, FLP-106 (64.6% ADN, 23.9% H_2O and 11.5% low volatile hydrocarbon fuel) also showed higher performance in comparison to hydrazine. The following year, Wingborg (2006) studied the interaction between ADN and water and reported that ADN was more hygroscopic in comparison to AN, where solubility of ADN and AN in water at 20 °C was reported to be 78.1 and 65.5%, respectively . Besides, atmospheric relative humidity should be below 55% to prevent ADN (critical relative humidity: 55.2%) from absorbing moisture during the handling, storing and processing stages.

Recently, Rahman et al. (2017) have reported the successful prilling and coating of ADN with polystyrene and HTPB in a toluene mixture, using ultrasound sonication. The ADN prilled and coated with 5 wt% of polystyrene with graphene shows excellent resistance to water absorption with only 10% increase in mass after 2 h of water uptake experiments. However, the thermal decomposition of the product remains to be a subject of future study.

Similarly, Gronland et al. (2006) fabricated a reactor for the decomposition of ADN-based liquid monopropellant and used alumina as the catalyst support material. They proposed the overall chemical reaction of ADN consisting of 64.3% ADN, 24.3% water and 11.4% methanol assuming the formation of thermodynamic products as:

$$94H_2O + 33NH_4N(NO_2)_2 + 22CH_3OH \rightarrow 22CO_2 + 204H_2O + 66N_2, \quad (7)$$

whereas for similar composition without water the corresponding net equation is given as:

$$3NH_4N(NO_2)_2 + 2CH_3OH \rightarrow 2CO_2 + 10H_2O + 6N_2. \quad (8)$$

As shown in (8), the complete decomposition of ADN only releases carbon dioxide, water vapor and nitrogen gas which can be considered as a promising choice of "green" propellant with minimum impacts to the environment.

One of the projects funded by the European Union's Horizon 2020 programme is the "Rheform Project" which stands for *Replacement of Hydrazine for Orbital and Launcher Propulsion Systems.* As one of the participating research centers in the Rheform Project, Negri (2017) tested the ignition of ADN (LMP-103S and FLP 106) using catalytic igniters, where ceramic materials such as cordierite, aluminum oxide, magnesium oxide and silicon nitride were used to manufacture the monolithic supports. To increase the specific surface area of monolithic supports, a wash-coating layer was applied by immersing supports in colloidal solutions of aluminum, alumina or aluminum oxohydroxide. The authors reported that the high specific area of the catalyst support is beneficial to increase the surface of contact between the propellant and active phase.

Toxicity of propellants

An essential aspect of clean space mission is to use green and non-toxic propellants to replace toxic hydrazine-based propellants. Registration, Evaluation, Authorisation and Restrictions of Chemicals (REACH) regulation in 2011 has highlighted hydrazine as a substance of high concern and that its use will be limited or forbidden in future (Gotzig 2015). As such, greening of hydrazine-based space propulsion devices is highly recommended. The advantages of green propellants in comparison to hydrazine are as follows (Tanaka et al. 2011):

I. Lower toxicity which leads to cost reduction (operability improvement and safety).
II. Reduction in propellant consumption (due to higher specific impulse).
III. Reduction in power consumption of heaters to prevent propellant from freezing (lower freezing point).

Figure 5 shows the toxicity of propellants where the x-axis represents the oral median lethal dose (LD 50)—the dose required to kill half the subjects of the tested population after a specified duration, while the y-axis represents the carcinogenicity based on the evaluation of

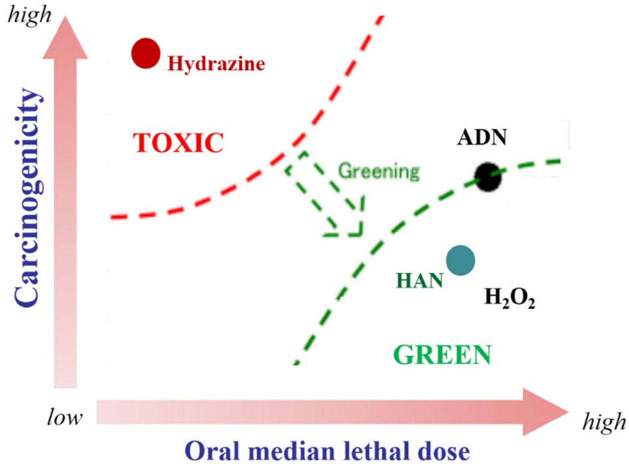

Fig. 5 Toxicity assessment of various propellants (Tanaka et al. 2011)

the International Agency for Research on Cancer (IARC) (Tanaka et al. 2011). On the upper left region, the smaller *x* value for hydrazine indicates that the propellant is acutely toxic, while its larger *y* value indicates its high carcinogenicity. As such, it can be seen that HAN, ADN and H_2O_2 appear to be green propellants with low carcinogenicity and low acute toxicity.

Conclusions

In-depth reviews from these studies indicate that green propellants have the possibility of replacing hydrazine-based propellants which impose distinctive environmental impacts. Ceramic materials have demonstrated their potential as structural materials of microthrusters through various microfabrication techniques.

Progress has been made over the last decade to study the characteristics and decomposition of H_2O_2 in ceramic microthrusters. There are still many opportunities for the application of green propellants (particularly, HAN and ADN) in ceramic microthrusters as only the proof of concept of HAN-based LTCC ceramic microthruster has been demonstrated. It is interesting to explore the combination of HTCC ceramic and HAN or ADN green propellant. In addition to that, further studies could be carried out to address the cracking issues reported in HTCC ceramic microthrusters. The two possible routes identified are to: (1) investigate the technique or approach to control the reaction rate of green propellant to mitigate rapid temperature rise and (2) explore alternative ceramic materials, e.g., silicon carbide and silicon nitride, with better thermal shock resistance.

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