

CONTROL OF LIQUID HYPERGOLIC REACTIONS IN MICRO-REACTORS USING DIFFUSIONAL MIXING

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Abstract: This paper presents the design, fabrication and initial testing of a silicon based micro-reactor used to study liquid hypergolic propellants. The study isolates the liquid-phase reactions and provides the first comprehensive measurements and analysis of the effect of diffusion based mixing on the interfacial reactions between the propellants under observation using temperature measurements as a measure of the amount of reaction occurring at the interface. It thus aims to provide a more in-depth analysis of the reactions that occur at initiation between the propellants.

Keywords: micro-reactors, hypergolic propellants, fast liquid-liquid reactions.

INTRODUCTION

Hypergolic bipropellants are oxidizer and fuel pairs that chemically react on contact, and are able to release enough heat to be able to spontaneously ignite without the aid of an external ignition source. Owing to their high-energy content, fast reactions occurring between the fluids and the lack of complex ignition systems, these propellants are highly suitable to power MEMS devices. Although these propellants have been used for decades in rocket engines, the ignition process involves a complex interrelation between physical and chemical phenomena which is poorly understood.

Moreover, as the hypergolic fuels, such as hydrazine, monomethylhydrazine (MMH) and unsymmetrical dimethylhydrazine (UDMH) are usually extremely toxic and often also carcinogenic, there is an urgent need to develop newer, safer fuels. A number of amines or amine-azides [1, 2] have recently been developed and tested as alternate fuels with tetramethylethylenediamine (TMEDA) being the most favored one [3] due to its similarity with MMH in many aspects as well as its lower toxicity [4]. To better develop these alternate fuels, a deeper understanding of kinetic mechanisms and reaction rates that occur during hypergolic combustion is thus required.

Traditional testing of hypergols has been usually carried out via either dropping of one of the hypergol pairs into the other [5], mixing of the hypergols together [6] or by impinging the reactants onto one another using injectors to recreate rocket conditions [7]. These types of experiments are usually plagued by variabilities caused by the droplet size, the manner in which the droplets impacts the other reactant or the

manner in which the impingement takes place. Most importantly the mixing of the reactants, which is hard to control in these tests, always plays a large role in the tests. These tests are rarely, if ever, able to isolate the early liquid-phase reactions from the gas-phase reactions that occur later on and lead to ignition. This study aims to utilize micro-reactors to control the mixing between the reactants as well as isolate the early liquid-phase chemistry and concentrate on the point of initial contact.

Unlike macro-scale experiments, fluid flow on the micro-scale is dominated by laminar flow which ensures that the mixing at the interface between the two fluids is through diffusion alone. If the flow conditions inside the reactor are chosen, either through design of the device or through specific flow conditions, such that the Péclet number (non-dimensional number comparing the rate of advection of a physical quantity to the rate of diffusion for the same physical quantity) is high then the mixing at the interface will be negligible. Thus the interface between the two reactants can be kept kinetically stable as well as be sharply defined. Another major advantage of using micro-fluidic systems is that they utilize very low quantity of reagents. It is thus much safer to carry out the experiments with toxic and corrosive reagents in these systems rather than using traditional macro-fluidic testing systems.

FABRICATION

Micro-fluidic channels are mostly fabricated using techniques used in the micro-electronics industry. The most popular material to fabricate micro-fluidic devices is now poly di-methyl siloxane (PDMS) as devices made from the polymer can be easily batch

processed using standard soft lithography and mold replica techniques [8]. These channels are able to provide optical access as well as be robust enough to be used in most micro-fluidic applications. Owing to the fact that the present study uses extremely corrosive reagents, PDMS based micro-fluidic channels could not be used and instead silicon-based reactors capped with Borofloat glass were fabricated instead. The silicon substrates can be easily coated with a coating of silicon di-oxide, silicon nitride or any other metal to avoid compatibility issues between the reagents and the substrate used for fabricating the fluidic channels. It should be noted that no surface reaction or a change in the surface of the reactors was noticed while using the reagents and thus the silicon was left uncoated in the micro-reactors.

Unlike the PDMS micro-channels, where the inlet tubing is introduced into the channels using through holes made into the polymers itself using conventional machining, the silicon channels are more difficult to micro-machine in the same manner. Thus the micro-reactors were designed to be attached to an external manifold where they would be held into place by a compression seal. The inlet and exhaust ports for the reactor would be thus etched into the silicon from underneath and then have these ports line-up with the ports in the manifold.

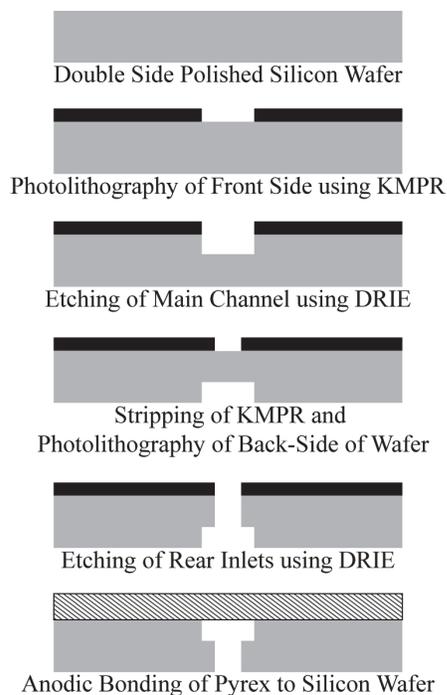


Fig. 1: Fabrication process used for the micro-reactors.

A detailed schematic of the fabrication process is described as shown in Fig. 1. Double sided polished

silicon wafers were used as the substrate and for the sake of uniformity all the substrates used for fabrication were 4" diameter, 500 μ m thick, n-type silicon wafers with a resistivity ranging between 2 and 5 Ω -cm. Micro-chem KMPR, an i-line high contrast, epoxy based photoresist was used for the photolithography process. This resist was chosen as it was able to provide high etch selectivity with better adhesion and higher thickness compared to the more popular photoresists (Shipley 1827 and 1810).

The silicon wafers were then etched anisotropically using deep reactive ion etching (DRIE) using a standard Bosch process. The process was carried out on an Alcatel Speeder 100 and used sulfur hexafluoride (SF_6) as the gas to generate the plasma to attack the silicon, while using octafluorocyclobutane (C_4F_8) as the source gas to generate the chemically inert passivation layer which helps in etching vertical side-walls as well as to achieve a high aspect ratio for the etch. For every cycle of the DRIE process, the SF_6 was flowed for 3 seconds at 300 sccm while the C_4F_8 was flowed for 1.5 seconds at 300 sccm. Oxygen (O_2) gas was also flowed into the chamber between the SF_6 and C_4F_8 pulses at 100 sccm for 1 second. An LF generator was used for the process initially but it was noticed that the bottom of the etched reactor was not flat and instead had a deep ridge in the middle (Fig. 2(a)). The etch process was then modified to use an RF generator instead of the LF generator, while keeping the rest of the process parameters the same. The resulting etch resulted in perfectly flat bottom in the etched channels (Fig. 2(b)) and thus ensured the flow in the reactors was deterministic by having a uniform rectangular cross-section throughout the length of the reactor. The overall etch rate for the process was approximately 6 μ m/minute.

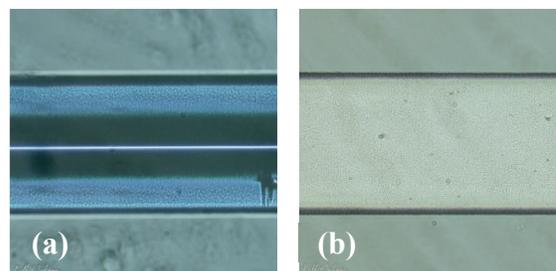


Fig. 2: Top-view of etched main channel using (a) LF generator and (b) RF generator for the DRIE

The photoresist was then stripped from the wafer and the inlet and exhaust ports were etched in a similar fashion on the back-side of the wafer. The photoresist was stripped once again and wafers were then cleaned using a standard piranha solution (3:1

mixture of concentrated sulfuric acid and 30% hydrogen peroxide solution). The silicon wafers were then bonded to Borofloat glass wafers using anodic bonding. As a final step the bonded wafer was diced into individual micro-reactors.

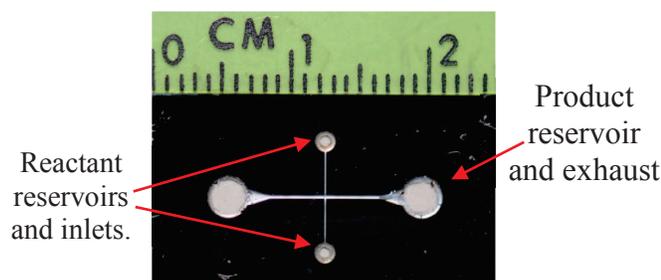


Fig. 3: Fabricated stagnation-flow micro-reactor with glass side up.

The micro-reactor (Fig. 3) used in the present study was designed such that it created a stagnation flow between the two reactants within the main channel. Thus there were two inlet ports and two exhaust ports for each reactor. Each of the reactors had a main channel width of $240\mu\text{m}$, a depth of 55 to $60\mu\text{m}$ and an overall length of about 1cm .

The manifold for the micro-reactors was fabricated from SS316 to account for the highly corrosive reagents under study. The ports to the micro-reactors were sealed using Kalrez o-rings while outside fluidic connection were realized using Swagelok tube connections. Apart from solving the problem of providing a way to pump the propellants into reactors while avoiding the use of hypodermic tubing, these manifolds also provided a secure way of collecting the toxic fumes and the products from the reactions between the hypergols.

EXPERIMENTAL

All experiments were run with the micro-reactor mounted glass-side up onto the stainless steel manifold and the entire assembly studied under an upright microscope (Nikon Eclipse LV100) (Fig. 4). The diffusion reaction-interface inside the micro-reactor was visualized using a high speed camera (Phantom V 7.3) attached to the microscope. The reactants were introduced into the reactor by connecting the inlet ports to high pressure stainless steel syringes using Teflon tubing. For high precision control of the flow of the reactants into the reactor, the syringes were controlled using two independent high pressure syringe pumps (Harvard Apparatus PHD4400). Temperature measurements were made simultaneously along with the visualization of the flow by introducing fine-wire thermocouples into the

exhaust reservoirs of the main channels. These thermocouples were carefully placed at the center of the exhaust ports to measure the temperature changes at the reaction zone. An exothermic reaction inside the micro-reactor was indicated by a rise in exit temperature of the products. The exhaust ports were connected to a water trap as well as a high velocity exhaust fan further downstream so that the fumes and the products from the reactions could be easily contained.

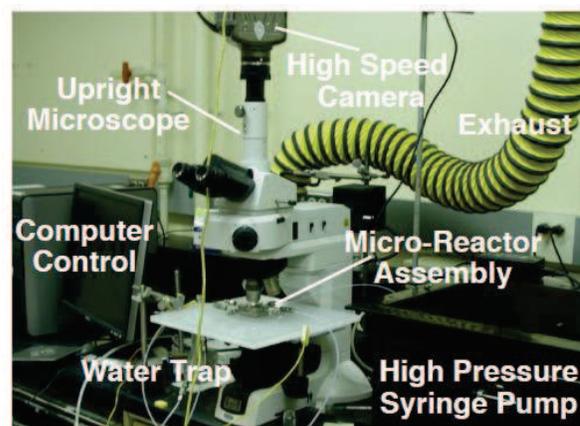


Fig. 4: Experimental setup showing reactor assembly under an upright microscope.

Experimental runs were made using 90% nitric acid acting as the oxidizer and with TMEDA being the complimentary hypergolic fuel. The nitric acid was diluted with distilled water which helped in reducing the reaction rates of the reactions that occurred in the micro-reactors as well as providing for a range of conditions to be run. Most of the micro-reactors were tested using flow rates such that the Reynolds number of the flow in the main channel ranged between 7 and 196. These flow rates implied a mean residence time ranging between 0.76ms and $27\mu\text{s}$ per channel width.

RESULTS AND DISCUSSION

A laminar flow was observed within the flow reactors even when reactions were occurring at the interface between the two hypergols. Thus flow in the micro-reactors was deterministic and the diffusion across the interface was easy to control. As seen in Fig. 5, the concentration, as expected, had an effect on the exit temperatures with their being a higher rise in temperatures when higher concentrations of nitric acid were used. More interestingly, the flow rates of the reactor had a large effect on the reaction that occurred within the micro-reactor. The exit temperatures of the products were seen to clearly rise with an increase in flow rates.

Even though the residence times within the reactor

were decreased by increasing the flow rates of the reactants, more reaction seems to be occurring within the reactor. Owing to the small scales of the flow, the system is diffusion controlled and thus the reaction at the interface between the hypergols is controlled by the diffusion of the reactants across the interface. It has been shown by previous studies that the species concentration gradients tend to increase with an increase in fluid flow rates of the reactants into a micro-reactor [9]. This increase in species concentration gradients leads to an increase in diffusion of reactant molecules across the interface which in turn causes a larger reaction to occur. Thus the increase in exit temperature with increasing flow rates can now be explained by an increase of this diffusion of reactant molecules across the interface. Using flow rates of the reactants and in-turn the diffusional mixing that occurs at the interface as a control mechanism, the reaction that occurs at the interface between the hypergols can thus be easily controlled giving control to energy release from the propellants making it easier to harness the energy in a controlled manner for MEMS applications and other devices. These results and more complete models and analysis of the hypergolic reactions in the micro-reactors are currently in progress [10].

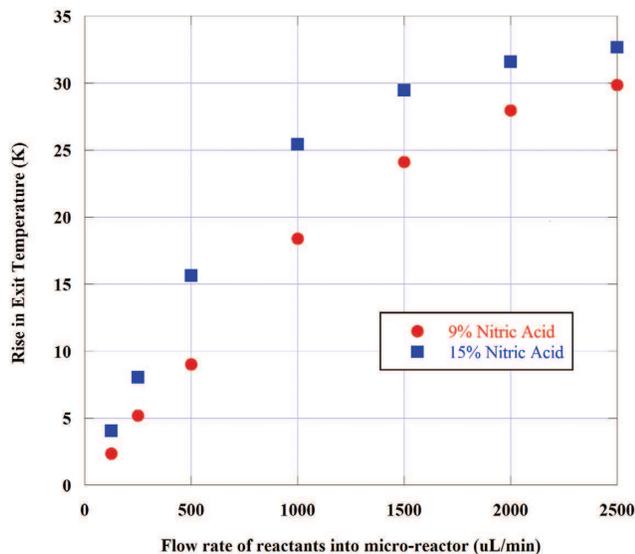


Fig. 5: Change in exit temperatures of products in micro-reactors with increasing flow rates of reactants

CONCLUSION

Micro-reactors have been successfully designed, fabricated and tested to study fast liquid-phase reactions that occur between hypergolic propellants. A close dependence has been shown between flow-rates and reaction occurring between the hypergols in the experiments and thus it is possible to control the

amount of reaction that occurs at the interface between the two reactants. Although this study was used to study only hypergols, the micro-reactors can be used to study any fast liquid-liquid reactions and control reactions that occur at the interfaces.

ACKNOWLEDGEMENTS

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