Toughening Graphite for Rocket Nozzle Durability

I first employed graphite nozzles when I was developing my "A" series of ammonium nitrate (AN) propellant formulations. The combustion temperature of these formulations, which contained an appreciable percentage of aluminum powder, was a lot hotter than steel nozzles could contend with. I had been using steel nozzles for all my sugar propellant motors, which worked well and rarely suffered much erosion. The combustion temperature of sugar propellants (in the range of 1370-1450° Celsius) is a little below the melting point of low-carbon steel (1500-1540°C). My *A24* propellant, which has an aluminum content of 17%, has a (ideal) combustion temperature of 2420° Celsius. As such, the choice of graphite for a nozzle (or nozzle insert) was an obvious one, as the melting point of graphite is 3600° Celsius. More recently I have been developing ammonium perchlorate (AP) based propellants. These are also hot burning formulations containing between 7 and 10 percent aluminum powder. Characterizing these propellants necessitates a nozzle with a constant (non-eroding) throat diameter.

Graphite has a long and proven history of usage as an effective rocket nozzle material, particularly for high temperature propellants such as metalized APCP. Graphite is easy to machine, as it is fairly soft, but has the drawback of being messy, as the graphite turnings are comprised of a small granules as well as a fine powder which tends to spread all over. Graphite can be easily scratched or chipped inadvertently. I generally use isomolded superfine graphite rod, which has the highest density and strength of commonly available graphite [1].

Another drawback to the use of graphite as a rocket nozzle is that graphite is a form of carbon. Carbon readily burns in the presence of free oxygen or oxidizing compounds. As long at the rocket exhaust products contain no oxygen or other oxidizing agents, this is not a problem. Non-metalized propellants that utilize graphite as a nozzle material should be designed to be slightly fuel-rich. This can be readily checked using PropPEP to ensure free oxygen is not one of the combustion products. Metalized propellants pose a different, however related, problem. The high combustion temperature tends to break down the steam (H_2O) in the exhaust. The resulting oxygen reacts with the graphite nozzle leading to erosion of the throat. Carbon dioxide (CO_2) also serves as an oxidizing agent that contributes to nozzle chemical erosion. Nearly all graphite nozzle erosion is a result of chemical attack [2]. Mechanical impingement resulting from presence of aluminum oxide (Al_2O_3) particles in the exhaust stream does *not* cause throat erosion. In fact, the higher the percentage of aluminum in the propellant, the less erosion occurs (attributed to decreased concentrations of H_2O and CO_2 in the exhaust stream).

Graphite nozzle erosion, or more exactly, *throat erosion*, is problematic for rocket experimenters for a couple of reasons. The first, and obvious, reason is that erosion of the nozzle makes it limited to a single use. The nozzle can be used for additional firings if having a larger throat diameter is acceptable. The throat can simply be re-drilled a bit larger. However, this is an ad-hoc approach to mitigating the problem. The more significant drawback to throat erosion is that it makes characterizing a propellant more difficult and adds uncertainty to the results (as we do not know the true erosion rate). For characterizing a propellant the throat diameter should be constant.

I eventually came up with an effective method of *toughening* a graphite nozzle that has, in testing, demonstrated that throat erosion is largely eliminated. Graphite is porous, with the porosity ranging typically from 12% (isomolded superfine) to 21% for medium extruded. The volume not filled with graphite is filled with air. My method displaces the air and replaces it with polymer. This polymer serves not only to greatly reduce erosion, but to make the graphite stronger and harder, in particular, more resistance to chipping and scratching. Another benefit is that the nozzle insert is less difficult to clean after firing. Slag consisting largely of hard aluminum oxide coats the nozzle flow surfaces. This material is rather hard to remove. I have had success with cleaning the slag by soaking the graphite insert (or entire nozzle) in CLR (calcium remover) for three or four days. The CLR infiltrates the porous slag then weakens it. The slag can then be carefully chipped away using a tiny cold chisel. A toughened nozzle allows the slag to be chipped away with less effort (and suffers less scratching), as the slag does not penetrate the filled pores of toughened graphite.

My method for toughening a graphite nozzle is outlined below.

1. Machine the graphite nozzle (or insert) to blueprint dimensions [*Figure 1*]
2. Wash the nozzle thoroughly with soap and water
3. Dry the nozzle fully using a hair dryer, or allow to air-dry completely
4. Add oil-based polyurethane [3] varnish to a suitable container (with lid) such that the level will completely immerse the nozzle [*Figure 2*]
5. Place the nozzle into the polyurethane, close lid to prevent evaporation of the solvent
6. Allow to soak for 2-3 days [4]
7. Remove the nozzle, then transfer the varnish into a suitable container that will fit inside a vacuum bowl (if necessary) [*Figure 3*]
8. Immerse the nozzle fully
9. Place in vacuum bowl, then draw vacuum of at least 25 inches of Hg.
10. Bubbles will be seen emanating from the nozzle, as air is drawn from the pores [*Figures 4 & 5*]
11. Once bubbles have stopped forming, nozzle is removed from vacuum bowl and wiped fully with suitable cloth
12. Allow to dry fully (2 or 3 days)

I can only speculate as to why throat erosion of a toughened nozzle is held in check. I have speculated that the polymer provides protection through the process of pyrolysis. A very thin layer of gases resulting from pyrolysis of the polymer flows over the throat protecting the graphite from the harmful oxidizing compounds present in the exhaust stream.

To date, I have not done *multiple* firings on a nozzle that has been toughened. There has been zero erosion after a *single* firing. As a future follow-up project, I plan to investigate the amount of erosion that occurs as a result of multiple firings of a toughened nozzle.

Another future plan is to toughen the graphite stock *prior* to machining. This would be of benefit as the stronger and harder toughened graphite would be less prone to chipping or other damage during the machining process. An unknown to such an approach would be if all the air in the graphite can be drawn out, and the depth to which the varnish will infiltrate the graphite.

Notations

[1] Available from graphitestore.com

[2] *Chemical Erosion of Carbon–Carbon/Graphite Nozzles in Solid-Propellant Rocket Motors*, Piyush Thakre∗ and Vigor Yang, JOURNAL OF PROPULSION AND POWER, Vol. 24, No. 4, July–August 2008

[3] Must be oil-based. Do not use water-based varnish

[4] It may be possible to eliminate this "pre-soaking".

Figure 1 – Machined graphite nozzle throat insert

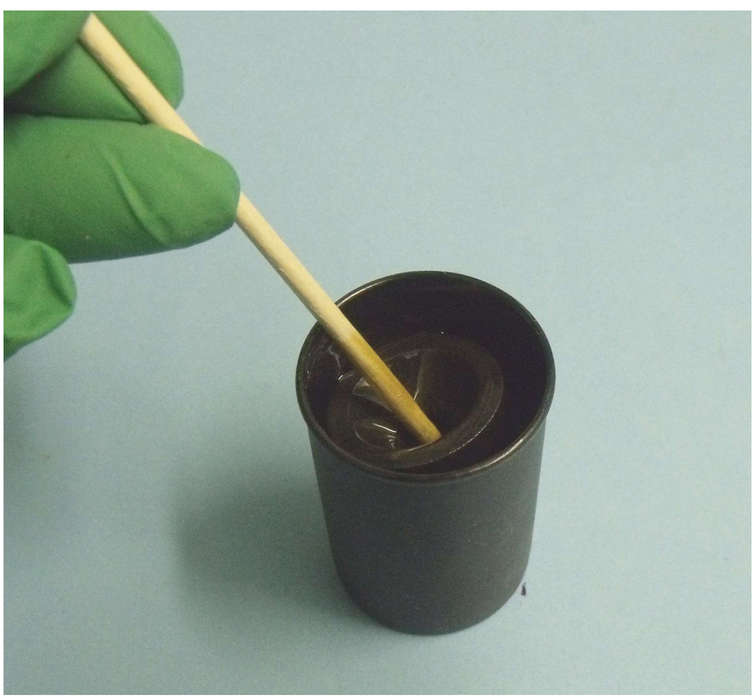

Figure 2 – Insert conveniently fits inside a 35mm film canister

Figure 3 – Insert placed (sideways) into a shallow container and filled with varnish, then placed inside vacuum bowl

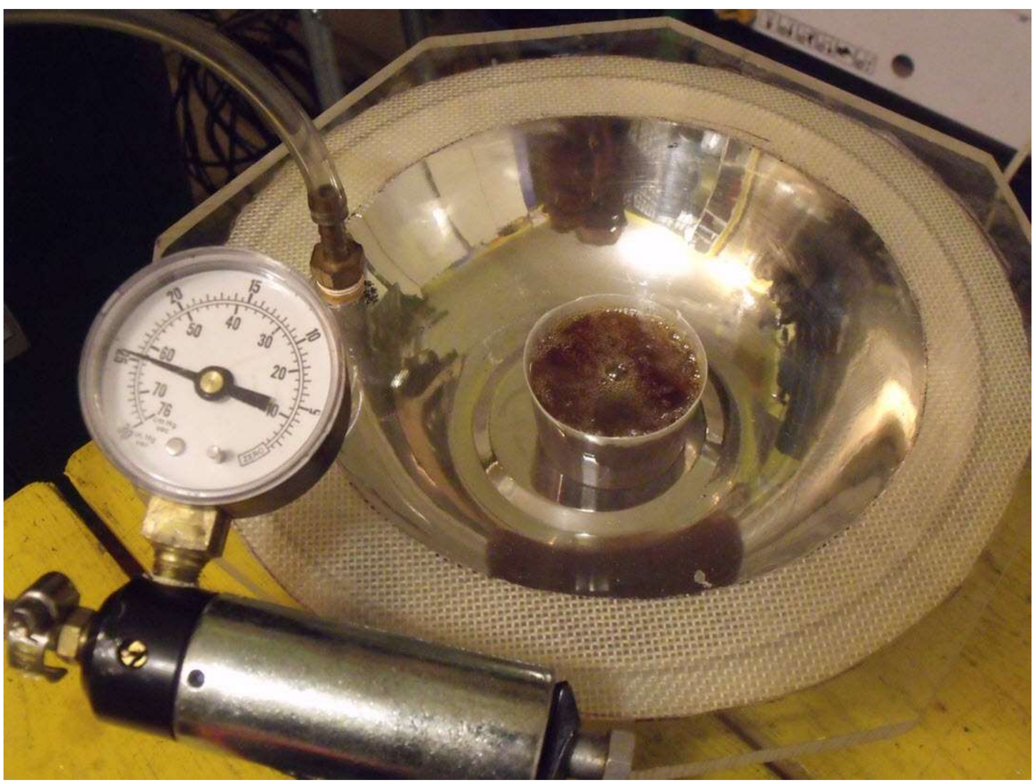

Figure 4 – Lid is placed on vacuum bowl, then air evacuated to 25 in.Hg. Bubbles rise from insert as air is drawn from pores

Figure 5 – After approximately ½ hour, all air is removed from pores and bubbling ceases