2015

Graphitic Oxide and Graphene as Enhancers for Energetic Mixtures

Luhrs, Claudia C.; Vilardi, Nicholas; Menon, Sarath

Monterey, California. Naval Postgraduate School

https://hdl.handle.net/10945/57921

NAVAL POSTGRADUATE SCHOOL

NAVAL RESEARCH PROGRAM

MONTEREY, CALIFORNIA

GRAPHITIC OXIDE AND GRAPHENE AS ENHANCERS FOR ENERGETIC MIXTURES

by

Claudia C. Luhrs

Nicholas Vilardi, Sarath Menon, GSEAS

FY14-FY15

Prepared for:
OPNAV 403
CDR Karen Dallas

EXECUTIVE SUMMARY

Project Summary

The aim of this project was to study the effects of using graphene (G) and graphitic oxide (GO) as additives in energetic reactions. The thermite oxidative reaction was selected as the initial reaction to test. The rationale behind the use of GO and G as additives originates from the fact that GO has the ability to release its oxygen groups when heated at low temperatures and graphene burns off generating volatile species at moderate temperatures. GO or G were added to thermite mixtures and heated to promote the aluminum oxidation in the presence and absence of iron oxide, in inert and oxygen containing atmospheres. The changes in mass were recorded using thermogravimetric analysis while the heat flows involved were determined by calorimetry. A mass spectrometer analyzed the evolved gases. The solid crystalline precursors and byproducts were identified using x-ray diffraction techniques and their microstructural characteristics and identity studied using microscopy and spectroscopy. Evidenced by the byproducts generated, the thermogravimetric/calorimetric study of the processes and the microstructures observed, the addition of GO or G to aluminum accelerates the oxidation reaction. A mechanism for the different oxidation steps when additives are used was proposed. In addition to the thermite reaction, GO and G were also used as additives in the combustion of propellant mixtures. Testing was conducted to determine changes in visible smoke and flame distance from the propellant during burn.

Background

The United States Navy has ambitious goals for reducing energy consumption in the coming years. To achieve the desired goals will require a multi-faceted approach, which will necessarily include improvements in energy efficiency. This provided the motivation for this research, the purpose of which was to study the effects of adding graphitic oxide (GO) and graphene (G) to materials known to experience exothermic reactions during heating. The question to be answered: Could these materials enhance the exothermic reactions, either by making them more exothermic, or by inducing reactions at lower temperatures? A positive response will justify the future use of the additives in other fuel mixtures.

The primary means of conducting this analysis was through experimental research: mixing of graphitic oxide and graphene with materials known to react exothermically. Thermite mixtures of aluminum and iron oxide were selected as the first type of energetic reaction to test and the study focused on analyzing their energy changes through calorimetry. Complete characterization of the materials microstructure and composition both prior to and after heating (including byproducts) was also conducted to ensure a complete understanding of the observed mechanisms.

A secondary means of conducting this analysis was through the mixing of graphitic oxide with a known propellant. In this case, the purpose was a test of practicality and feasibility. Characterization of the propellant was also conducted, though not to the same level of detail as with the thermite mixtures.

Findings and Conclusions

The following are the conclusions and milestones that resulted from the research conducted during the process of completing this project.

Milestones

There were numerous milestones achieved and lessons taken away from the research conducted to determine the advantages of utilizing GO or graphene as additives in combustible mixtures. The most significant are summarized below.

Graphite oxide (GO) and graphene (G) were successfully prepared. The former was generated from graphite flakes treated in a controlled highly oxidant environment. The latter was produced when GO was treated thermally at 1000°C.

The samples weight changes and heat flows of the process were studied *in situ,* employing a simultaneous TGA/DSC apparatus while being heated from RT to 1050°C (thermite) or 900°C (propellant). The evolved gases from the processes were identified by mass spectrometry. All the solid precursors and byproducts microstructural and crystalline features were identified by the use of electron microscopy and x-ray diffraction techniques.

The hypotheses proposed at the beginning of this research were tested; both graphitic oxide and graphene could be used as additives to enhance the thermite reaction studied. Graphene presents a much higher improvement in terms of the heat flow achieved when compared to graphitic oxide when enough oxygen is contained in the process atmosphere.

The makeup of GO, approximately 50 percent carbon and 50 percent oxygen groups attached to its surface, increases the amount of oxygen in the reaction crucible through the release of the oxygen groups at temperatures close to 200°C. However, since the temperature of oxygen release happens at much lower temperatures than the one at which aluminum melts (660°C), only a slight amount of oxygen coming from GO gets to interact with the aluminum particulates. In contrast, graphene does not have the ability to free oxygen at low temperatures, but instead burns off in oxygen containing atmospheres to produce CO_2 in a rapid process that promotes the swift release of gases. The interaction of the latter with the melting aluminum removes the thin layer of aluminum oxide already present on the aluminum particles surface, exposing unreacted aluminum and increasing its oxidation rate. In contrast, when the process is carried out in inert atmosphere instead of an oxygen containing one, GO tends to lose the oxygen group to form graphene at low temperature and the remnant graphene reacts with aluminum to form the corresponding carbides.
In air environments, or those including at least 20 percent oxygen, graphene, due to its high thermal conductivity in conjunction with its high surface area (close to 600 m^2/g) and geometry, seems to be a great prospect for improving exothermic reactions.

The most significant finding was the mechanism by which, in the thermite mixtures studied in oxygen, the effect of the additive was to release gases that promote the bursting of aluminum shells, exposing more Al surface area and increasing the oxidation rate. The purpose of the thermite reaction is the rapid oxidation of one metal, due to the rapid reduction of another material. This project demonstrated, unequivocally, that the additives employed could enhance the existing mixtures, or even possibly serve as substitutes of the reduction agent. Moreover, the use of GO and G do not have a downside from the environmental point of view since they burn off completely without generating solid byproducts.

Recommendations for Further Research

Further study of systems such as F76 or biofuel is recommended. Based on the thermite reaction outcomes presented herein, the use of graphene instead of GO could prove advantageous.