International Journal of Scientific Engineering and Technology (ISSN : 2277-1581)
Volume No.3 Issue No.9, pp : 1189-1192 1 Sep 2014

Preliminary Design of Multifunctional Structural-Energetic Materials for High Density, High Strength and Release of High Enthalpic Energy

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Abstract: Reactive materials, such as thermite-like metal-metal oxide mixtures, intermetallic mixtures and combustible metals are being studied as candidates for binary energetic materials. During the past decade, there are several studies to use these reactive materials to design dual functional structural-energetic materials. Most of the earlier studies resulted in low strength, low density structural energetic materials, with low released enthalpic energies upon initiation of the reaction. In this paper procedures are developed to design hybrid dual functional structural energetic materials, with specified high density, high strength and capability to release high enthalpic energies following the initiation of the reaction of reactive material components

1. Introduction

Usually the choice of aerospace structural materials depends on their strength characteristics and their strength to weight ratios. The term strength implies resistance to expected loads during the service life of the structure including resistance to fatigue loads, corrosion and extreme loading conditions. Thus, basically the structural materials have a single function of resisting loads experienced during the service life of the structure. However, it is desirable to design materials that are capable of offering more than one basic function of strength. Very often, the second function is the capability to provide functions of a sensor and control actuators. In this paper, the second function does not include sensing or control actuation. The second function is to include energetic characteristics. Thus, the dual functions of the material are the structural characteristics and energetic characteristics. These materials are also known by other names such as the reactive material structures or dual functional structural energetic materials [1-7]. Specifically the selected reactive structural materials include mixtures of selected metals and metal oxides that are also known as thermite mixtures; reacting intermetallic combinations and oxidizing materials. Techniques to synthesize these structural energetic materials or reactive material-structures (RMS), with desired strength and energetic characteristics, is an open research area.

The reactive materials that form the foundations for RMS or reactive material-structures are usually classified into 3types: metal/metal oxide mixtures (thermites); metal/metal mixtures (intermetallics); and combustible metals (metal to metal oxide reaction) [1,2]. These materials are being studied for many applications. One of the application is to design projectiles that can penetrate a specified target by using the function of high density and structural strength. Following the penetration, then use the second function of the multifunctional material. The second function is the capability to react and release the large heat content, resulting from the exothermic reaction. Another reason for the study of these reactive materials is to prospect for these materials in space, including asteroids, and use these materials as fuels for interplanetary exploration.

2. Background:

The different reactive materials that form the foundations for the reactive material-structures or structural-energetic material form three types of reactive material mixtures, without techniques for synthesis and/or binding techniques. These are as follows [1-3].

- Metal/metal oxide mixtures (thermites);
- Metal/metal mixtures (intermetallics); and
- Combustible metals (metal to metal oxide reaction).

To discuss the possible design of reactive material structures (RMS) for specific use, some of the characteristics of a few selected thermite mixtures, intermetallic mixtures and combustible oxidizing metals are as follows [1].

I Thermite Mixtures:

Reactive Materials Mixture	Density of Mixture g/cc Kelvin	Mixture Reaction Temperature Calories/	Heat of Reaction Gram
1.3Mg + B2O3	1.785	6,389/3,873	2,134
2Al + Ni2O3	4.045	5,031/3,187	1,292
2Y +Ni2O3	4.636	7,614/3,955	1,120
2Al + Fe2O3	4.175	4,382/3,135	945
4Al + 3MnO2	4.014	4,829/2,918	1,159
Al + KclO4	2.5		3000

II. INTERMETALLIC MIXTURES

Reactive Materials Mixture (Inter-Metallic)	Density of Mixture g/cc	Mixture Reaction Temperature (Kelvin)	Heat of Reaction Calories/gram
2B + Ti	3.603	3,043	1,320
Mo + 2Si	4.582	3,498	207
2B + Hf	8.232	3,945/3,653	742
Al + Ni	5.165	2,362/1,910	330
Hf + C	9.084	4,441/4,222	315
Al + Ta	9.952	1,011	57
2C + Th	8.169	3,073	247
2B + Ta	10.36	2,666	

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III. Combustible Oxidizing Metals

Metal to Metal Oxide Combustion	Density of Mixture g/cc	Reaction Temperature (Kelvin)	Heat of Reaction Calories/gram
Hf / HfO2	11.4	2,495	1,491
Ta/Ta2O5	16.6	3,390	1,390
Al / Al2O3	2.7	933	7,422
Mg / MgO	1.5	923	6,241
Mn /Mn3O4	7.3	1,519	2,012
Mo / MoO3	9.1	2,896	1,856
Nb /Nb2O5	8.57	2,750	2,443
Ti /TiO2	4.5	1,693	4,714
Y /Y2O3	4.47	1,799	2,819
W /WO2	19.3	3,695	767

3.Objectives

The objective of the paper is to design a reactive material structure (RMS), with a tensile strength of at least 100,000 pounds per square inch, comparable to the strength realized in steel; a high enthalpic energy of the reactive material structure (RMS) of at least 1,200 calories per gram of the RMS; and a the density of the RMS to be at least 7.8 grams per cc as seen in materials such as steel. These specifications are only for purposes of illustration. It is possible to formulate other specifications depending on the needs.

4. Design Procedure:

A review of the table of reactive materials that are listed illustrates that it is difficult to meet the combined goals of high density, high strength and high enthalpic energy/gram requirements, with a single thermite or a single intermetallics mixture. It is necessary to combine a thermite or an intermetallic with combustible metals and to assure that the reactions of thermite or the intermetallics provide the necessary condition for an RMS with selected goals of high density and high strength of steel while an enthalpic energy release is comparable to conventional energetic materials.

In the design, there are two different requirements. First requirement is that of density and structural strength. Most of the thermite-like metal-metal oxide mixtures have low density. Thus, to meet the density requirements, it is necessary to consider intermetallic mixtures. However, the intermetallic mixtures, usually release limited amount of enthalpic energy up on reaction. As observed in many tests, it is possible to initiate the intermetallic reaction [3] by supplying thermal energy or shock induced or assisted energy to the intermetallic mixture, to overcome the energy barrier for reaction of a chemical reaction [3]. However, the intermetallic reactions do not meet the specified goal of 1200 calories per gram of the released enthalpic energy. We have already ruled out the use of thermite-like metal-metal oxide mixture because of low density compared to the design objective of at least 7.5 grams/cc comparable to that of steel.

Thus, it is not possible to meet the design goals by using either only the thermite mixture alone or the intermetallic mixture alone. The table on combustible metals offers high released enthalpic energy upon combustion of the metal. For example the combustion of aluminum to aluminum oxide has the potential to release 7,432 calories per gram of the material. Both for the design of the reactive material-structure (and later as fuel for planetary exploration, combustible or oxidizing aluminum is a very good choice.

However, it is very difficult to initiate the combustible metal reaction of aluminum. In many experiments of solid rocket propellant studies, there are several studies to incorporate aluminum, to increase the efficiency of the fuel. In many cases the aluminum did not oxidize. However incorporation of nano particle size aluminum met with some success [8]. Thus, we need to incorporate nanoparticle size aluminum. Thus, it is necessary to design a hybrid intermetallic-oxidizing metal based reactive material structure (HIOM) or a hybrid intermetallic-thermite mixture-oxidizing metal (HITOM). The motivation is to use the heat released by either the reaction of intermetallic mixture or the reaction of thermite mixture to initiate the reaction of the combustible metal. Of course the density of the hybrid HIOM or HITOM needs to be high (to meet the specifications). The intermetallic mixture of Hf +2B along with Ta has the potential to increase the density of the reactive mixture significantly. The heat release, following the reaction of Hf + 2B is of the order of 742 calories per gram. Then, the next question is as follows? Is this amount of released heat sufficient to initiate the combustible metal reactions such as that of aluminum to aluminum oxide or tantalum to tantalum oxide? Thus, as needed it may be necessary to include thermite mixtures, such as, Mg and$B_2 O_3$; or Al and$Ni_2 O_3$. The incorporation of a thermite mixture has the tendency to lower the overall density of the hybrid reactive material but can release heat or enthalpic energy of the order of 2,134 and 1,292 calories per gram that has the potential to initiate the oxidation reaction of aluminum and tantalum and release a significantly large amount of enthalpic energy, of the order of 7,422 calories per gram (of aluminum..

The first category is the HIOM or Hybrid Intermetallics and oxidizing metal based reactive material structures. In selecting these materials the intermetallic reaction releases some heat at temperatures that have the potential to initiate the metal oxidation reaction. Primarily the density requirements force us to include high-density materials such as Hf and Ta. By including even small amounts of aluminum we can realize a significant amount of energy release during the oxidation of aluminum to Al2O3 (7,422 calories per gram of Al). Some selected design combinations are as follows:

HIOM Designs:

- Hf + 2B ` 33%
  Al 20%

  Ta 47%

  Combined Density 11g/cc

  Energy released 2,344 calories/gram

- Hf + 2B 33%
  Al 20%

Hf 47%

Combined Density 8.65g/cc

Energy released 2,394 calories/gram

- Hf + 2B 50%
  Nb 50%

Combined Density 8.4 g/cc

Energy released 1,594 calories

HITOM Designs:

- Hf + 2B ` 33%
  Al 20%

  Ta 27%

  1.3Mg +$B_2\ O_3$ 20%

Combined Density 8.1g/cc

Energy released 2,531 calories/gram

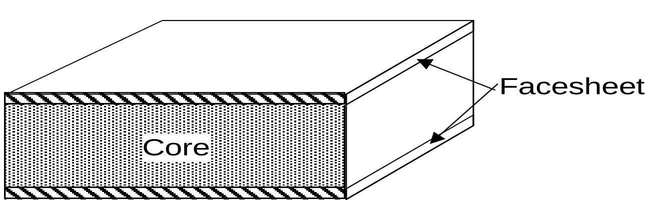
These are only a few designs. It is possible to design many different combination of hybrid reactive materials, depending on the specified need, restrictions on the cost and environmental considerations.

4. Synthesis of HIOM and HITOM and Laboratory Testing

The component parts of both HIOM and HITOM consist of intermetallic mixtures and nano-particles of aluminum and tantalum. A binder such as Teflon, PBAN or epoxy can be used. If we need more strength the metal components can be divided into face sheets of a composite and cores consisting of nano-particles for facilitating oxidation of metals. This has the potential to decrease the released total enthalpic energy of HITOM or HIOM.

For a first series of laboratory testing DTA tests can be used to assess the reaction initiation and enthalpic energy released. In studying intermetallic mixtures and thermite type of mixtures DTA tests have been success fully used [2, 9]]. The composite construction is discussed below. In practice electrical or laser-based initiation techniques are possible to start the reaction process following other operations such as the impact and penetration of selected targets.

5. Composite construction of Hybrid Reactive Material Structure:



Sandwich panel

The next class of reactive material combination is by sandwich construction that has not been tried before. The core is made of selected thermites, nano-metallic aluminum particles, and polymer binders. Thermites are selected for high-energy release capability. However, high-energy release capability is associated with low-density mixture. Thus, it is necessary to select face sheets of oxidizing metal or rolled sheets of high-density intermetallics such as nickel and aluminum. In a sandwich construction, the face sheets resist the tensile loads.

Figure 1: Sandwich Panel

The core has to elongate with the strain of the face sheet without experiencing any core failure. This is the role that is played by the polymer. The polymer, such as Teflon, also assists in rapidly propagating the reaction when the chemical reaction is initiated. At present the thermites that are being considered for the core are Al + KClO4 and/or Mg +B2O3. The polymers that are being considered are Teflon, DELRINand other polymers such as ESTAN, PBAN that are used with conventional energetic materials.

6. Structural Strength Analysis, Tests and Demonstration of Selected Practical Applications

Preliminary design of hybrid design of reactive material structure is only a first step. For any analysis of strength (or impact and penetration followed by the initiation and complete reaction to release the enthalpic energy), it is necessary to obtain the constitutive relationships under finite deformation conditions and use of these constitutive relationships, with other equations of motion, for structural strength-numerical analysis under impact and penetration operations, using numerical procedures. The constitutive relationships can be obtained through expensive gas gun tests or bench top laser driven shock tests or by the use of modified density functional theory [3, 10-16]. Then, results of the laboratory tests on reactions can be used assess non-initiation through structural operations, such as impact and penetration and a desired reaction following the needed structural operations.

Another important step is the initiation of the reaction of the reactive materials, of the structural-energetic materials. There are several techniques that are available for thermal ignition techniques, including electrical and laser-induced ignition. However, shock induced or shock assisted initiation of reaction is still an active research area and needs additional research

7. Conclusions

In this paper, options and procedures for preliminary designs of hybrid reactive material-structures were discussed. In cases of reactive material structures, the objectives were to achieve a high density (or a specified minimum density) of the reactive material structures and a specified release of the enthalpic energy, upon a successful reaction. The preliminary design was based on the use of available knowledge of known thermite types of mixtures, intermetallic mixtures and combustible metals. It is necessary to follow the preliminary designs with laboratory tests, techniques to determine the constitutive relationships under finite deformations, structural strength analysis, structural strength tests and practical demonstration of the design objectives.

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