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THEORETICAL ENERGY RELEASE OF THERMITES, INTERMETALLICS, AND COMBUSTIBLE METALS †

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ABSTRACT

Thermite mixtures, intermetallic reactants, and metal fuels have long been used in pyrotechnic applications. Advantages of these systems typically include high energy density, high combustion temperature, and a wide range of gas production. They generally exhibit high temperature stability and possess insensitive ignition properties. For the specific applications of humanitarian demining and disposal of unexploded ordnance, these pyrotechnic formulations offer additional benefits. The combination of high thermal input with low brisance can be used to neutralize the energetic materials in mines and other ordnance without the "explosive" high-blast-pressure events that can cause extensive collateral damage to personnel, facilities, and the environment. In this paper, we review the applications, benefits, and characteristics of thermite mixtures, intermetallic reactants, and metal fuels. Calculated values for reactant density, heat of reaction (per unit mass and per unit volume), and reaction temperature (without and with consideration of phase changes and the variation of specific heat values) are tabulated. These data are ranked in several ways, according to density, heat of reaction, reaction temperature, and gas production.

INTRODUCTION

Exothermic reactions between a metal and a metal oxide (thermite) and between metallic elements (intermetallic), as well as the combustion of metals (metal oxidation reactions), are extremely useful sources of energy production and material synthesis for numerous applications. For example, the thermite welding process was first demonstrated in 1898 and continues to be the most frequently used method for the field welding of railroad track.[1, 2]

Other applications for thermite reactions include: thermite torches for underwater and atmospheric cutting and perforation; electronic hardware destruct devices; additives to propellants and explosives for increased performance; pyrotechnic switches; airbag gas generator materials; reactive fragments; high-temperature-stable igniters; free-standing insertable heat

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sources; devices to breach ordnance cases to relieve pressure during fuel fires; and methods of producing alumina liners *in situ* for pipes.

Applications for intermetallic reactions include: consumable port covers for ramjet engine inlets; tracer compositions for munitions; ramjet fuels; self-ejecting combustible plumes for large-area heating; ignition aids for thermites; thermal battery heat sources; incendiary projectiles; delay fuzes; additives to propellants to increase burn rate without significant decrease of specific impulse; and shaped-charge liners.

Metal fuels have been used as: additives to increase shock sensitivity of explosives; additives to increase explosive blast effects; fuel-air explosives; additives to both solid and liquid propellants to increase density impulse; methods of controlling combustion instability in solid propellant rockets; additives to solid and liquid fuels for ramjets to increase range; and fuels in numerous pyrotechnic devices.[2-22]

Thermite, intermetallic, and metal fuels (with an oxidizer) can be ignited via a thermal impulse from a hot-wire, exploding bridgewire (EBW), or semiconductor bridge (SCB) igniter as well as by laser impingement, mechanical methods, or shock initiation.[12, 23-29] Many of these formulations are stable at high temperatures and are insensitive to the effects of moisture, corrosion, friction, spark, shock, contaminants, and variations in composition[15]. Clearly, these types of exothermic reaction mixtures provide the output for a wide variety of engineering applications with a large choice of ignition methods.

CALCULATIONS

The "traditional" thermite reaction is taken as the reaction of a stoichiometric mix of aluminum and magnetite (Fe_3O_4) reacting exothermically to completion with the products being alumina (Al_2O_3) and iron. Many other thermite mixtures exist; many of these, as well as intermetallic and metal-oxidation reactions, are surveyed in this paper. Some of these reactions produce little or no gas. Others produce significant amounts of gaseous products. The reactant composition can be chosen to produce solid, liquid, and/or gaseous products as required for the particular application.[6, 30, 31]

Tables 1a through 1f list the theoretical maximum density (TMD) of the reactants, the adiabatic reaction temperature without and with taking into account the heats of phase changes, the state of the products, the amount of gas produced referenced to the total mass of the reactants (or products), and the heat of reaction based on the mass and volume of the reactants for a selection of exothermic thermite reactions. The same information for intermetallic reactions is listed in Tables 2a through 2f. In the field of intermetallic reactions, boron, carbon, and silicon are usually considered metallic.[15] In the present study, sulfur is also included. In these tables the reactions are first listed alphabetically and then ranked in descending order according to reactant density, heat of reaction (per unit mass and per unit volume of the reactants), reaction temperature, and moles of gas produced per unit mass. Analogous values (metal density and heat of reaction with respect to the mass and volume of the metal) for metal-oxidation reactions are listed in Tables 3a through 3d. Physical, thermochemical, and reaction data are taken from references 13, 14, 17, 18, 28, and 32 through 47.

The heat of reaction is calculated assuming complete adiabatic reaction of the reactants starting at 298K. The increase in temperature is calculated using the average specific heat over the temperature range from 298K to the adiabatic reaction temperature. If phase transitions (solid-solid, solid-liquid, or liquid-gas) occur over that temperature range, the adiabatic reaction temperature is calculated taking into account the heats of those transitions and using the average specific heats for each temperature range between transitions. This calculated temperature is an upper limit for the ideal case of complete reaction and no energy losses.

In most of the calculations reported in the open literature, the adiabatic reaction temperature is calculated without taking into account the heats of the phase transitions. This leads to erroneously high temperatures. For instance, for "traditional" thermite ($8Al + 3Fe_3O_4$) the adiabatic reaction temperature with no phase transitions taken into account is calculated as 4057K. In contrast, with the solid-solid, solid-liquid, and liquid-gas heats of transition included, the adiabatic reaction temperature is more accurately calculated as 3135K. Similarly, for Ti + 2B, the calculated adiabatic reaction temperature drops from 3710K to 3498K. Measured reaction temperatures are in reasonable agreement with the calculated values. Temperatures ranging from 2800K to 3000K have been measured for $8Al + 3Fe_3O_4$, while that for Ti + 2B has been measured in the range of 3150K to 3300K.[15, 47, 50]

An accurate calculation of the adiabatic reaction temperature is important for determining whether the reaction is likely to be self-propagating. A strong indication that the reaction is self-propagating is if at least one of the product species is brought to its melt temperature.[43] Another indication that a reaction is self-propagating is an adiabatic reaction temperature greater than 2000K.[17] (Reactions which are not self-propagating under normal conditions may become so when initiated by a high-power stimulus, such as a high-energy shock. Self-propagation can also be promoted by preheating the reactants to a high temperature.[43]) It should be noted that, because the effect of phase changes on the product temperature takes a finite time, the initial temperature rise may control the diffusion and reaction rates before the temperature drops due to the phase changes.[28]

The reaction temperature is also a guide as to which materials are suitable for a given application. For some applications, such as cutting through metal, high temperatures are required. For others, such as air-bag inflation, low-temperature products are desirable.

DISCUSSION

For engineering applications, the "optimal" exothermic mixture is dependent on several factors which include: energy per unit mass (or volume depending on the requirements of the application); chemical stability of the reactants and products at normal operating temperatures; chemical compatibility of the reactants and products with other materials present in the application; toxicity of the reactants and products; reaction rate; ease of processing; availability of the reactants; reaction temperature; state of the products; and cost.

From Tables 1 and 2, thermite and intermetallic compositions can be selected to produce solid, liquid, or gaseous reaction products as required for a particular application. In situations where gas production is undesirable, such as obturated systems, applications for which it is desirable to control the reaction rate by conduction rather than convection, or systems which may be adversely affected by pressure variations, solid and liquid products are more suitable. However, in order to perform mechanical work, rapidly convey the product (as in a torch-type output), or inflate items such as airbags, the production of gases is required.

Similar compromises apply for the selection of metal fuels. Desirable properties for metal fuels are a high heat of combustion per unit mass of metal (or of the metal and the oxidizer for some applications), a high density, and low melt and vaporization temperatures. Table 3 contains several properties of importance. Ideally one would select boron or beryllium based on their high energy content. Unfortunately, low combustion efficiency and toxicity, respectively, limit the application of these metals. In general, the wide use of aluminum in propellant, pyrotechnic, and explosive formulations is because of its many desirable properties. Most other metals have applications in systems requiring very specific properties. For example, zirconium is used where ignition sensitivity and high reaction rates are required, while copper is used when a good heat conductor is necessary.

SUMMARY

Numerous thermite and intermetallic energetic compositions exist that can be used for a wide variety of engineering applications. Metal combustion reactions are also of great utility. A comprehensive list of these materials and their energetic properties is presented here. Comparison to experimentally measured reaction temperatures shows reasonable agreement with the calculated adiabatic reaction temperatures when phase changes are taken into account. The properties tabulated in this report provide a useful guide for choosing exothermic formulations for engineering applications.

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NOTE:

The tables referenced in the paper are available under separate cover.