TSS Material Selection

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Note: It is generally accepted that fundamental energetic material characteristics, such as the calculations shown here are appropriate for UUR. Once integrated into a device, the guidance of the system takes precedent.

Introduction

Energetic materials (EMs, explosives, pyrotechnics, propellants) provide high-power output of high temperature reaction products. These products can be solid, liquid, or gaseous during reaction or after the products have equilibrated with the surroundings. For example, high explosives typically consist of carbon, hydrogen, nitrogen, and oxygen bonded within a single molecule, and produce almost exclusively gaseous products. Conversely, intermetallics consist of physical mixtures of metals and metalloids, and produce almost exclusively condensed products. Other materials such as pyrotechnics and propellants have intermediate behavior. All energetic materials react in a self-propagating manner that after ignition, does not necessarily require energy input from the surroundings. The range of reaction velocities can range from mm/s for intermetallics, to km/s for high explosives.

Energetic material selection depends on numerous requirements specific to the needs of a system. High explosives are used for applications where high pressure gases are necessary for pushing or fracturing materials (e.g., rock, metal) or creating shock waves or air blast. Propellants are used to produce moderate-pressure, high-temperature products without a shock wave. Pyrotechnics are used to produce numerous effects including: high-temperature products, gases, light, smoke, sound, and others. Thermites are used to produce heat, high-temperature products, materials, and other effects that require condensed products. Intermetallics are used to produce high-temperature condensed products and materials, with very little gas production. Numerous categories of energetic materials exist with overlapping definitions, effects, and properties.

Europa Lander Terminal Sterilization System Material Selection

Material selection for the Europa Lander Terminal Sterilization System (TSS) is based on several requirements. High explosives and propellants are immediately eliminated for consideration due to the gaseous nature of reaction products that would result in undesirable pressurization and/or venting of the vault. Intermetallics, thermites, and pyrotechnics, and mixtures thereof, are thus considered for selection. Examples and descriptions of these reactions are shown in

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Table 1.

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Table 1. Examples of intermetallic, thermite, and pyrotechnic reactions and effects.

Material class	Example reactions	Phase during and after reaction	Qualitative description
Intermetallic	$Ti + 2B \rightarrow TiB_2$ $Ni + Al \rightarrow NiAl$	solid/liquid (during) solid (after)	High temperature, no gas products, conductive burn
Thermite	$2Al + Fe_2O_3 \rightarrow Al_2O_3 + 2Fe$ $2Al + 3CuO \rightarrow Al_2O_3 + 3Cu$	liquid/gas (during) solid (after)	Gas during reaction, sparks, conductive-convective
Pyrotechnic	$2Ti + KClO_4 \rightarrow TiO_2 + KCl$ $3Zn + C_2Cl_6 \rightarrow 2C + 3ZnCl_2$	liquid/gas (during) solid/gas (after)	Fast reaction, convective burn, violent, can produce air blast

Intermetallics are first evaluated because they can result exclusively in condensed products and thus result in the lowest gas production and resultant pressurization of the vault. Examples of these reactions are shown in Table 2.

Table 2. Example intermetallic reactions in order of energy per mass. Adapted from Fischer and Grubelich.[1]

Reaction	Density	T, no phase change	T, incl. phase change	Product phase	Gas production	Gas production	H	H
	g/cm3	K	K	0	mol/100 g	g/g	kJ/g	kJ/cm3
2B + Ti	3.603	3710	3498	liquid	0	0	5.52	21.63
2Be + C	1.995	1932	1932	solid	0	0	3.90	7.78
Al + 2B	2.607	2251	1252	l-g	0-2.1	0-1	3.10	8.12
C + Ti	3.754	3644	3523	liquid	0	0	3.08	11.55
2Si + V	3.429	3341	2023	s-l	0	0	2.93	10.04
2B + Zr	4.926	3783	3673	liquid	0	0	2.86	14.06
2B + V	4.187	2960	2960	s-l	0	0	2.81	11.76
B + Ti	3.922	3559	2452	l or g	0 - 1.7	0 - 1	2.73	10.71
2B + Nb	5.875	2793	2793	solid	0	0	2.19	12.89
Al + Pd	7.072	2725	2653	liquid	0	0	1.37	12.09
C + Hf	9.084	4441	4222	s-l	0	0	1.32	11.97
2B + Ta	10.36	2766	2766	solid	0	0	1.03	10.71
C + Zr	5.276	3800	3800	solid	0	0	1.90	10.04
C + V	4.499	2121	2121	solid	0	0	1.60	7.20
Al + Ni	5.165	2362	>1910	s-l	0	0	1.38	7.15
Al + Pt	11.63	3379	3073	liquid	0	0	0.90	10.50

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Based on the energy content and widespread use of the Ti/2B reaction, this reaction is considered and studied using the thermochemical equilibrium code Cheetah.[2] Cheetah can be used to calculate the available energy from the formation of TiB_2 by the following reaction:

Ti + 2B → TiB2, (1)

which results in a enthalpy value of –3.6 kJ/g (when products cool to 500 °C) and an adiabatic flame temperature of 3190 K. This enthalpy value can be used for heat conduction modeling that shows that conduction is too limiting for a gasless reaction to be used. This directs the material search to thermites that could be used to form gaseous products and result in high-velocity hot condensed products.

Thermite evaluation is conducted in a similar manner to intermetallics. Examples of thermite reactions are shown in Table 3.

Table 3. Example thermite reactions in order of energy per mass. Adapted from Fischer and Grubelich.[1]

Reaction	Density	T, no phase change	T, incl. phase change	Oxide product phase	Metal product phase	Gas production	Gas production	H	H
	g/cm3	K	K			mol/100 g	g/g	kJ/g	kJ/cm3
$3Mg + B_2O_3$	1.785	6389	3873	l-g	liquid	0.4981	0.2007	8.93	5.00
$3Be + B_2O_3$	1.85	3278	2573	liquid	s-l	0	0	6.86	12.69
$2Be + MnO_2$	3.882	6078	2969	liquid	gas	0.9527	0.5234	6.64	25.77
$10Al + 3I_2O_5$	4.119	8680	3253	gas	gas	0.6293	1	6.22	25.61
$4Li + MnO_2$	1.656	3336	2334	liquid	l-g	0.4098	0.2251	5.85	9.69
$2Mg + MnO_2$	2.996	5209	3271	liquid	gas	0.7378	0.4053	5.53	16.57
$2Al + Ni_2O_3$	4.045	5031	3187	liquid	l-g	0.465	0.2729	5.41	21.88
$3Be + Fe_2O_3$	4.163	4244	3135	liquid	l-g	0.1029	0.0568	5.36	22.31
Be + CuO	5.119	3761	2820	s-l	liquid	0	0	5.11	26.15
$4Al + 3MnO_2$	4.014	4829	2918	liquid	gas	0.8136	0.447	4.85	19.46
$10Y + 3I_2O_5$	4.638	12416	4573	gas	gas	0.4231	1	4.79	22.21
$2Al + MoO_3$	3.808	5574	3253	l-g	liquid	0.2425	0.2473	4.70	17.90
$2Y + Ni_2O_3$	4.636	7614	3955	liquid	gas	0.5827	0.342	4.69	21.73
$3Mg + Fe_2O_3$	3.224	4703	3135	liquid	l-g	0.2021	0.1129	4.64	14.97
Mg + CuO	3.934	6502	2843	solid	l-g	0.8186	0.5201	4.61	18.14
$10Al + 3V_2O_5$	3.107	3953	3273	l-g	liquid	0.0699	0.0356	4.57	14.20
$4Mg + Fe_3O_4$	3.274	4446	3135	liquid	l-g	0.1369	0.0764	4.32	14.15
$4Y + 3MnO_2$	4.69	7405	5731	gas	gas	0.811	1	4.28	20.05
$8Al + 3Co_3O_4$	4.716	3938	3201	liquid	l-g	0.2196	0.1294	4.23	19.97
$2Y + MoO_3$	4.567	8778	4572	gas	liquid	0.6215	1	4.20	19.20
2Al + 3CuO	5.109	5718	2843	liquid	l-g	0.54	0.3431	4.08	20.82
$10Y + 3V_2O_5$	3.97	7243	3652	l-g	gas	0.213	0.4181	4.07	16.15
$2Al + Fe_2O_3$	4.175	4382	3135	liquid	l-g	0.1404	0.0784	3.96	16.51

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2Y + 3CuO	5.404	7668	3124	liquid	l-g	0.7204	0.4577	3.88	20.95
2Al + 3AgO	6.085	7503	3253	l-g	gas	0.7519	0.8083	3.75	22.83

Based on the widespread use of the 2Al/3CuO reaction, this is considered and studied using the thermochemical equilibrium code Cheetah.[2] Cheetah is used to calculate the available energy from the formation of Al_2O_3/3Cu by the following reaction:

$$2Al + 3CuO \rightarrow Al_2O_3 + 3Cu, \qquad (2)$$

which results in a enthalpy value of –3.8 kJ/g (when products cool to 500 °C) and an adiabatic flame temperature of 2840 K. In contrast to the intermetallic of Ti/2B, the thermite reaction of 2Al/3CuO results in a much more energetic reaction.

Since pressurization of the vault is a potential concern, calculations are performed to investigate a tailored heat source in which a mixture of Ti/2B : 2Al/3CuO could be used to result in some advection of reaction products, but while tailoring the energetics to prevent over-pressurization. Calculations of a variety of mixtures are shown in Table 4.

Table 4. Calculations showing characteristics of Ti/2B : 2Al/3CuO mixture.

		At adiabatic flame T			At 500 °C		
Ti/2B : 2Al/3CuO ratio	Density	T, adiabatic	Total Gas	Total Condensed	H at 500 °C	Total Gas	Total Condensed
	g/cm3	K	g/g	g/g	kJ/g	g/g	g/g
100:0	3.516	3190	0.00	1.00	-3.60	0.00	1.00
90:10	3.627	3140	0.08	0.92	-3.62	0.00	1.00
80:20	3.745	2750	0.17	0.83	-3.64	0.00	1.00
70:30	3.871	2750	0.18	0.82	-3.67	0.00	1.00
60:40	4.006	2750	0.19	0.81	-3.69	0.00	1.00
0:100	5.062	2840	0.23	0.77	-3.83	0.00	1.00

From the results in Table 4, it is apparent from the columns describing the gas and condensed product fractions that this strategy could potentially be used to tailor the combustion and product characteristics of the heat source.

The use of an intermetallic heat source would result in a gasless heater while a thermite heat source would result in a torch. In the event that intermetallic and/or thermite heat source does not meet the mass requirements of the Europa Lander, the strategy of consuming some portion of the lander as fuel could be considered. This results in a mass savings due to the simple fact that not as much fuel has to be carried as part of the heat source. A more important benefit may be that the act of consuming portions of the Lander may result in more effective heat transfer through erosive burning of internal surfaces. By consuming some of the Lander, there is also less inert mass to heat. Finally, more efficient oxidizers may be able, or be required, to be used due to expected combustion inefficiencies with low-surface area structures.

There are a number of potential oxidizers (materials that provide electronegative elements, O, F, Cl) that could be used for the concept of consuming some portion of the Lander as fuel, but salts of perchlorate, ClO_4^- are obvious choices. Based on the widespread use of potassium perchlorate ($KClO_4$), this is considered and studied using the thermochemical equilibrium code Cheetah.[2] Cheetah is used to calculate the available energy from the combustion of Al/$KClO_4$ by the following reaction:

$$12Al + 3KClO4 \rightarrow 6Al_2O_3 + 3KCl, \qquad (2)$$

which results in a enthalpy value of –10.2 kJ/g (when products cool to 500 °C) and an adiabatic flame temperature of 3670 K. In contrast to both the intermetallic reaction of Ti/2B and the thermite reaction of 2Al/3CuO, Al/$KClO_4$ results in a much more energetic reaction with characteristics of an explosion. For this reason, PTFE (poly(tetrafluoroethylene) is suggested as a potential binder and burning rate modifier. Calculations for Al/$KClO_4$/PTFE are shown in Table 5.

Table 5. Calculations showing characteristics of Al/$KClO_4$/PTFE. PTFE (poly(tetrafluoroethylene) is suggested as a potential binder and burning rate modifier.

				At adiabatic flame T			At 500 °C		
Al, elemental	$KClO_4$	PTFE, Teflon	Density	T, adiabatic	Total Gas	Total Condensed	H at 500 °C	Total Gas	Total Condensed
			g/cm3	K	g/g	g/g	kJ/g	g/g	g/g
34.18	65.82	0.00	2.584	3672	0.42	0.58	-10.2	0.00	1.00
33.65	61.35	5.00	2.567	3495	0.48	0.52	-10.0	0.00	1.00
25.00	70.00	5.00	2.553	2781	0.57	0.43	-7.80	0.13	0.87

The calculations in Table 5 show that this mixture has a higher output than the intermetallic and thermite reactions suggested above. In addition, if the mixture is deliberately formulated to be fuel-lean, (e.g., the third entry in the table, 25:75:5 Al/KClO4/PTFE) some of the Lander structure could be used as fuel and mass efficiency could be improved. Some fuel will have to be carried in the TSS, and it is extremely unlikely that the Lander structure could be used solely as fuel. This approach is extremely specific to the integrated design (i.e., TSS + Lander) since some of the Lander is used as fuel and would likely require extensive experimentation to determine its viability.

Conclusion

Energetic material selection for the Europa Lander TSS is based on numerous factors. Due to long thermal conduction times, it is unlikely that an intermetallic reaction alone can be used to heat the interior structures. A thermite torch, a pyrotechnic torch, or a combination is likely to be the most viable option. This may include using some portion of the structure of the Europa Lander Vault and/or TSS as fuel. In addition to this potential efficiency gain, the TSS could also perform another function on the

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Lander. This may include contributing to the structure (known as a structural energetic material) or contributing to the radiation shielding. The materials used in the TSS must be selected to provide the appropriate compromise of combustion velocity while maintaining a low enough pressurization rate of the Vault. The approach to performing this should be by selecting a mixture of fuels (e.g., Al, Ti, B, Mg, etc.) and oxidizers (CuO, $KClO_4$, Bi_2O_3, MnO_2, $LiClO_4$) that provide the appropriate balance of gaseous and condensed products. Further calculations taking these considerations into account followed by experiments to inform system-level considerations should be performed as designs of the TSS are generated.

1. Fischer, S.H. and Grubelich, M.C., "Theoretical energy release of thermites, intermetallics, and combustible metals," *24th International Pyrotechnics Seminar* Monterey, CA, July 27-31, 1998.
2. Bastea, S., Fried, L.E., Glaesemann, K.R., Howard, W.M., Souers, P.C., and Vitello, P.A., "Cheetah 5.0 Users Manual," Lawerence Livermore National Laboratory, Livermore, CA, 2007.

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