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Reactive structure materials

Review Article

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Keywords:

Alloys, intermetallic phases, metal-polymer mixtures, reactive structure materials (RSM), warhead.

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Abstract

The effectiveness of lethal weapons is predominantly dependent on the overpressure generated and blast effect. Reactive structure materials (RSM) can be made of either metal-polymer mixtures or represent intermetallic phases. An example for a metal-polymer mixture is the system PTFE/W/Cu/Pb which shows higher penetration depth compared to the original PTFE/Al liner. The intermetallic phases (alloys) ZrW2 and HfW2 discussed in this review are very promising materials for use as reactive structure materials (RSMs). Both compounds have been shown to possess remarkable properties such as high melting temperatures, high densities, high hardness and high ignition energies on burning in air. The heats of combustion as well as the combustion temperatures have been calculated using the EXPLO5 code (version V6.05.02). ZrW2 and HfW2 can be prepared by melting the constituent elements in an arc-furnace. By cooling through peritectic phase lines above approximately 2000°C, samples of the nominal 1:2 composition were obtained as pure products (consisting of two phases, of which approximately 95% adopts the MgCu2 type structure and 5% the W structure). Both intermetallic phases are very dense and hard alloys which burn at a crash in air in a strong exothermic ignition reaction. Both intermetallic phases (alloys), ZrW2 and HfW2, are non-toxic.

I. INTRODUCTION

The effectiveness of lethal weapons is predominantly dependent on the overpressure generated and blast effect [1,2]. Therefore, if such weapons employed new secondary explosives which show a significantly higher performance, this would help to down-size the weapon system. However, if the weapon system is one which relies predominantly on the formation of fragments (fragmenting warheads, Figure 1) for its effectiveness, incorporating new high explosives – even those which show a significant improvement in performance - can only marginally help to improve the effectiveness of the weapon. In cases such as these, the key to improving the effectiveness could lie in enabling these weapons to generate chemically reactive fragments derived from structured reactive materials. The reason for this is that in conventional warheads up to 75 % of the mass is due to the non-reactive casing (steel casing). The use of chemically stable, but highly reactive materials as the casing instead of steel could help to solve this problem.

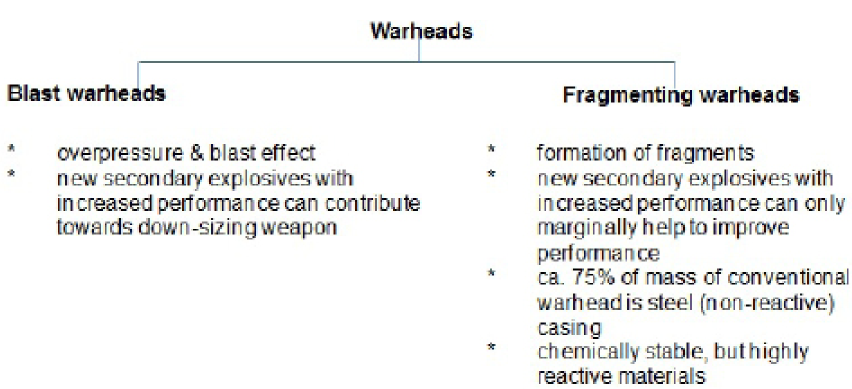

Fig. 1: Comparison of aspects of blast and fragmenting warheads (in addition to shaped charge warheads)

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Reactive materials (or structured reactive materials) are a new class of materials which are being investigated in weapons systems in order to increase the lethality of direct-hit or fragmentation warheads[1,2]. Reactive materials (usually thermites or thermite-like compositions) consist of two or more nonexplosive solid materials, which – crucially - do not react with each other until they are exposed to a strong mechanical stimulus[3-5]. After the appropriate stimulus has been applied, the solid materials undergo fast burning or detonation through which a large amount of energy (combustion, detonation) is released in addition to the kinetic energy. This is nicely illustrated by figure 2, which shows that using TNT as the explosive (30% mass percent), the use of a chemically non-inert casing can add an additional 40 – 70% of the total chemical energy produced by the explosive munition.

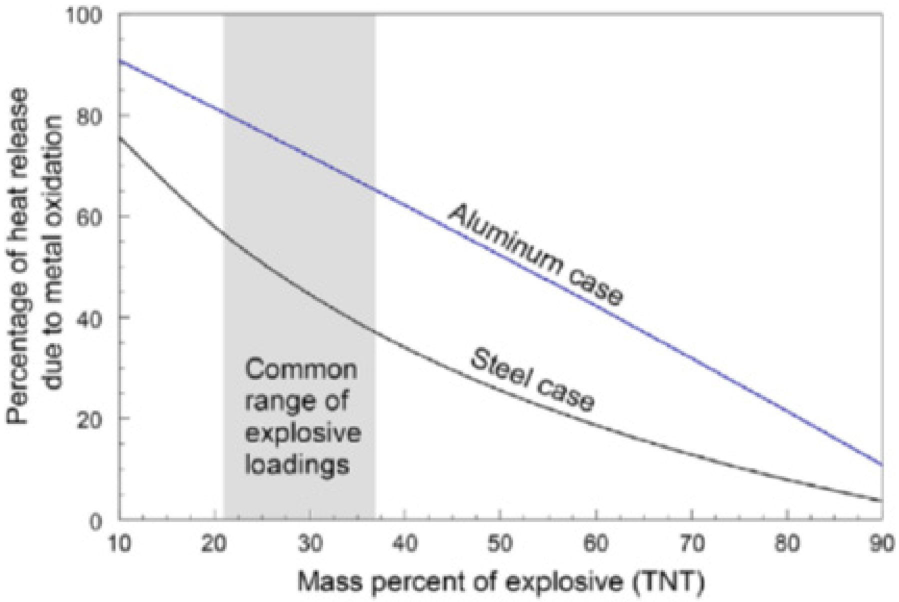

Fig. 2: Estimation of the contribution of the heat released if complete oxidation of a metal case occurs for a munition containing 30% TNT as explosive[2].

Consequently, fragments or projectiles made of reactive materials show a significantly larger damaging effect than non-reactive counterparts[6,7]. Structured reactive materials (SRM) are therefore expected to enhance the lethality of weapons, while maintaining or reducing the mass of the payload[8,9].

Possible candidate classes of materials under investigation as SRMs are[10]:

- Thermites[2]
- intermetallic phases (alloys)[2]
- metal-polymer mixtures (e.g. Al-PTFE)[3]
- composites (MIC, metastable intermolecular composites)

Such SRMs should possess the following properties:

- High density[11,12]
- High hardness
- Fast, highly exothermic reaction on hitting the target
- High mechanical strength (strong enough to act as structural component)
- Stable to survive extreme processes of launch, penetration
- Easily prepared, easily transported, safe to handle
- Unstable enough to allow reliable ignition when stimulus is applied
- Undergo rapid conversion from being a structural component to fine powder

Possible applications for RSMs are expected to include the following[13]:

- Kinetic penetrators (high density and high reactivity are important)
- Reactive fragments
- Reactive bullets
- Reactive armor
- Munitions casings

In order to begin the design of new RSMs, one initial selection criteria is the heat of oxidation of the metals since the greater the energy released the better. In this context, it is interesting to compare the heats of reactions of metals forming their corresponding fluorides, oxides, borides and carbides (Figure 3). Several trends become clear, such as that the fluorination and oxidation reactions of metals are generally substantially more exothermic than those forming metal borides or carbides (Figure 3). In addition, generally, the metals with lower densities show high gravimetric heats of reaction.

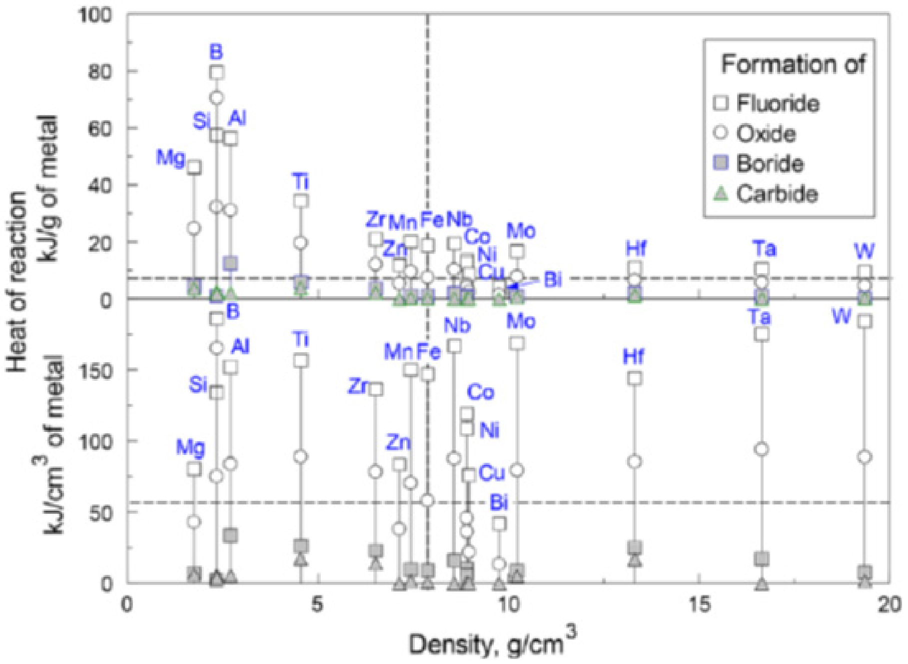

Fig. 3: Comparison of the heats of reaction for the formation of metal fluorides, oxides, borides and carbides[2].

Obviously, obtaining the maximum energy release from the formation of metal oxides is hugely important.

II. METAL-POLYMER MIXTURES

The topic of metal-polymer mixtures is usually associated with shaped charge (SC) liners or explosively formed projectiles (EFP). The reactive material liner is a kind of integrated solid energetic liner (and a special type of a structured reactive material) prepared by filling a metal powder in a polymeric binder, typically such as PTFE/Al and PTFE/Cu [14-18]. Such liners are usually produced by cold-pressing followed by a sintering process under an inert N2 atmosphere. Generally, the reactive material liner under the shaped charge effects can form a reactive jet which has a high enough velocity to enable it to penetrate the target, and subsequently, its violent chemical energy is released inside the penetration crater. A recent example of such a mixture is the system PTFE/W/Cu/Pb which shows higher penetration depth compared to the original PTFE/Al liner. Fig. 4 shows an example of a pressed and sintered PTFE/W/Cu/Pb SC liner. Some of the disadvantages of metal-fluoropolymer RSMs such as composites of Al/PTFE are that they often exhibit low densities and low strength. On example of such an Al/PTFE composite is 26.5 wt.% Al/73.5 wt.% PTFE which can be prepared by blending the powders followed by consolidation by compression at ca. 375°C to ensure structural integrity. Al/PTFE composites have also been prepared using nano Al.


Fig. 4: A pressed (left) and sintered (right) PTFE/W/Cu/Pb SC liner.

III. SILICON METAL-FLUORIDE COMPOSITES

A novel and still under investigation approach to reactive structured materials is the combination of Silicon with metal fluorides as reported by Dreizin *et al.*[19,20]. Silicon serves as a fuel in several pyrotechnic compositions, metal-fluorides were employed as oxidizers for micron-sized and nanometric silicon powders. The fluorides under investigation were BiF3 and CoF2:

$$Si + 4/x\ MF_x \rightarrow SiF4\ (g) + 4/x\ M\ (M = Bi, Co)$$

Unlike elemental Si, prepared composite powders ignited readily when placed as a coating on an electrically heated filament. Ignition of the composite with BiF3 as an oxidizer occurred at consistently lower temperatures than that of the composite with CoF_2. Results suggest that low-temperature fluorination and oxidation caused ignition for the composites with BiF3 as an oxidizer; apparent activation energy for reactions leading to ignition was close to 62 kJ/mol. For the composites with CoF_2 as an oxidizer, it is likely that ignition is associated with Si fluorination.

IV. INTERMETALLIC PHASES

In the selection of metal components for the preparation of an RSM alloy, there are many considerations which have to be undertaken, such as the melting point and density of the metal, toxicity, cost and of course the ΔHf,298 values for the corresponding metal oxides, to name but a few. A comparison of selected relevant properties for the metals Ti, Zr and Hf,[21,22] as well as of Ta, W, Re and Os are given in Table 1.

Table 1: Comparison of properties of one group of transition metals (Ti, Zr, Hf) and selected 5d transition metals (Hf, Ta, W, Re, Os) which are relevant when selecting candidate metals to act as components in new RSMs

metal/property	mpt. (°C)	density (g/cm3)	metal toxicity	ΔHf,298 metal oxide (kJ/mol)
Ti	1667	4.51	non-toxic	-940 (TiO2)
Zr	1857	6.50	non-toxic	-1100 (ZrO2)
Hf	2227	13.28	non-toxic	-1118 (HfO2)
Ta	3000	16.65	non-toxic	-2046 (Ta2O5)
W	3410	19.26	non-toxic	-835 (WO3)
Re	3180	21.03	non-toxic	-1128 (Re2O7)
Os	3045	22.61	non-toxic (OsO4 is highly toxic)	-386 (OsO4)

Two physical properties which are important determinants of the performance of a projectile are the hardness and density of the penetrator. This is because the ballistic limit velocity (i.e. the minimum velocity of a penetrator that is required to penetrate an object) drops significantly when the hardness of the projectile is greater than that of the target. Examples of recently investigated alloys are the systems Al-Zn-Zr and Al-U.

Figure 5 shows an arc-furnace AF92-1000. Two examples of intermetallic phases which have been recently reported and which may be two extremely interesting new examples are ZrW2 and HfW2 (Figure 6)[23,24]. These alloys were both prepared from the constituent metals (Zr and W; Hf and W), which were molten in an arc-furnace. The furnace was evacuated down to 10–4 mbar before re-filling the furnace with an argon atmosphere of 100 mbar prior to melting the metals. The melting process lasted 1–2 minutes, and was repeated about five times in order to obtain a homogeneous sample. In Figure 6, two reguli with an approximate mass of 5 g are shown.

Fig. 5: Arc-furnace AF92-1000. The long copper electrode can be moved up and down and turned around by a circle-movement. Between the electrode and the outer casing of the arc-furnace there is a tension of about 15 V, therefore, the operator uses isolating gloves.

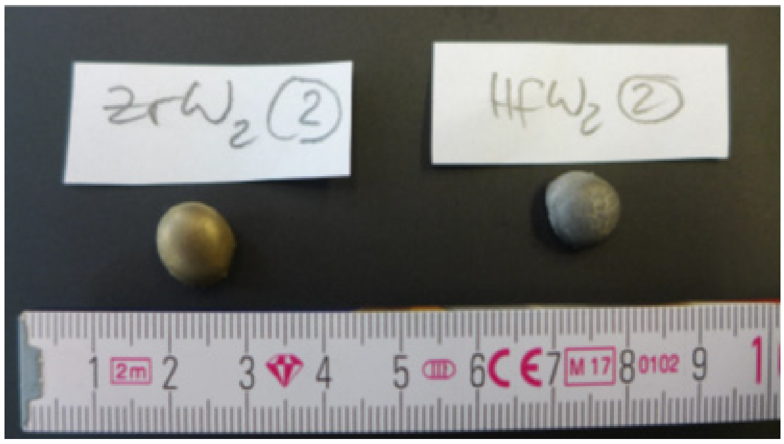

Fig. 6: Two samples of approximately 5 g of ZrW_2 and HfW_2. ZrW_2 has a more "golden" color, whereas HfW_2 is silvery-metallic.

Both ZrW_2 and HfW_2 possess a high-density ($\rho = 14.31$ g/cm^3 ZrW_2) and are very hard intermetallic compounds (Cu_2Mg-type crystal structure) that react/burn in highly exothermic reactions with air at high temperatures. Since both compounds have been shown to possess a remarkable combination of properties such as high melting temperatures, high densities, high hardness and high ignition energies on burning in air, these intermetallic phases could prove to be effective SRMs for warhead applications. A further important aspect of these compounds is that both alloys consist of non-toxic metals. Future research in SRMs will focus on materials with high mechanical strength, high density, and high energy density, that can rapidly convert from a consolidated structural material to fine powder with large surface area, be dispersed and then ignited to produce a large thermobaric blast.

The main advantages of ZrW_2 and HfW_2 as SRMs would be (Figure 6):

- ZrW_2 und HfW_2 have very high melting points (m.p. ZrW_2: 2210 °C, HfW_2: 2512 °C; both compounds melt peritectically).
- Both compounds react with air (O_2 and N_2!) at high temperatures in extremely exothermic reactions (Tables 3 and 4)
- The combustion products formed from the reaction with oxygen and nitrogen are the corresponding metal oxides and nitrides respectively (largely: ZrO_2 + W and HfO_2 + W), which are non-toxic (Tab. 1).
- ZrW_2 and HfW_2 are intermetallic phases, which are significantly harder than component metals. The values for the Vickers hardness HV 10 (in N mm^{-2}) are: Zr 140, Hf 228, W 385, ZrW_2 704, HfW_2 970 (Tab.3). The higher Vickers hardness value for HfW_2 in comparison with ZrW_2 may be the result of stronger bonding in the former. The hardness of HfW_2 lies between that of quartz and orthoclase!
- Both materials have an extremely high density. In the (110) plane of the Laves phases, all atoms are in contact with each other, therefore no higher density is possible.

Table 2: Heats of formation of the oxides and nitrides of the reactive tetravalent 4d and 5d transition metals Zr and Hf.

Metal M	Dioxide MO_2 (kJ/mole)	Nitride MN (kJ/mole)
Zr	-1100	-291
Hf	-1118	-374

Table 3: Hardness according to the Moh's and Vickers scale.

substance	Moh's scale	Vickers hardness (N•mm-2)
Diamond	10	10,000
Corundum	9	2035
Topaz	8	1567
Quartz	7	1161
Orthoclase	6	817
HfW2		970
ZrW2		704
W	7.5	385
Hf	5.5	228
Zr	5.0	140

Table 4: Combustion of metals and intermetallic phases (alloys) calculated with EXPLO5, isobaric combustion, 0.1 MPa

Fuel, mass-%	Oxidizer, mass-%	Oxygen balance	Tc / K	-Qc / kJ kg-1	Density of metal or alloy / g cm-3	Hardness (HV10)/ N mm-2
Steel, 35	Air, 65	0	1960	1703	7.85	160-210
Aluminum, 20	Air, 80	0	3581	4411	2.70	167
Zirconium, 39	Air, 69	0	3754	3143	6.49	140
Hafnium, 55	Air, 45	0	4322	2983	13.28	228
Tungsten, 46	Air, 54	6.6	2681	1918	19.28	385
ZrW2, 76	Air, 24	-7.6	3541	1545	14.31	704
ZrW2, 66	Air, 34	-3.6	3150	1572	14.31	704
ZrW2, 56	Air, 44	0	2767	1618	14.31	704
HfW2, 79	Air, 21	-6.7	3609	1458	17.03	970
HfW2, 70	Air, 30	-3.2	3061	1403	17.03	970
HfW2, 61	Air, 39	0	2716	1447	17.03	970

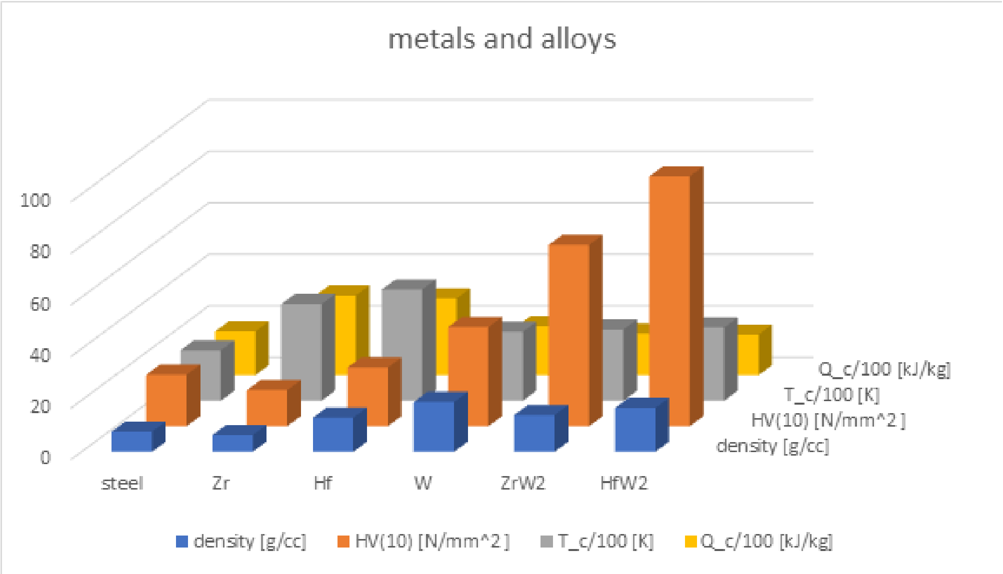

Fig. 6: Selected properties of metals and alloys

V. CONCLUSIONS

Reactive structure materials (RSM) can be made of either metal-polymer mixtures or represent intermetallic phases. An example for a metal-polymer mixture is the system PTFE/W/Cu/Pb which shows higher penetration depth compared to the original PTFE/Al liner. The alloys ZrW_2 and HfW_2 are examples for intermetallic phases. ZrW_2 and HfW_2 can be prepared by melting the constituent elements in an arc-furnace. By cooling through peritectic phase lines above approximately 2000°C, samples of the nominal 1:2 composition were obtained as pure products. Both intermetallic phases are very dense and hard alloys which burn at a crash in air in a strong exothermic ignition reaction. These materials are non-toxic.

VI. ACKNOWLEDGMENTS

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Article is dedicated to Professor Dr. Jürgen Evers on the occasion of his 80th birthday

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