Gasless Combustion-Driven Heating Elements for Materials Experiments in Space

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The novel concept of using gasless combustible mixtures as heating elements for materials processing in space and in ground-based microgravity facilities is presented. The unique properties of metal-sulfur combustible compositions (i.e., high flame temperatures, low ignition temperatures, liquid combus-tion products, nonporous charges, and gasless reactions) make them ideally suited for such heating applications. Heating ele-ments based on metal-sulfur combustion have an energy densi-ty more than order of magnitude greater than electrical batter-ies, can be easily integrated with processing samples, and can operate under high pressures and in different gaseous environ-ments. Demonstration prototypes of the gasless combustion-driven furnaces have already demonstrated peak temperatures close to 2300 K and heating rates above 200 °C/s.

The limits on available electrical power as well as weight and volume restrictions severely constrain the capabilities of furnaces available for materials science experiments on microgravity platforms. Heating elements utilizing gasless combustion described in this paper might dramatically extend the operational range of microgravity materials processing. The fact that chemical energy stored in a solid combustible mixture is converted directly to heat results in compact, high energy density heating elements and makes the material sample and heating charge a simple, self-contained assembly. The combustion-driven heating elements have an energy density more than an order of magnitude greater than electrical batteries and are expected to be capable of reaching peak temperatures exceeding 3000 K and heating rates more than 400 °C/s, far beyond the range of conventional electro-resistive furnaces.

Combustion of common, hydrocarbon fuels with oxygen is not suitable for space applications because of the hazards involved. Combustion of hydrocarbons generates very large quantities of hot gases that produce very high pressures if confined or undesirable thrust affecting the spacecraft if vented in space. However, if reaction occurs without the generation of gaseous products, the hazard can be eliminated and combustion can be used safely on board spacecraft or other microgravity platforms. At present, there are more than 500 solid-state combustion reactions known to generate little or no gaseous products [1]. These reactive systems are usually mixtures of metal and non-metal powders (e.g., Ti-C, Al-Ni, B-Ti, etc) and are commonly referred to in the literature as SHS (Self-Propagating High-temperature Synthesis) compositions. Most of the SHS reactions are used for material synthesis, though traditional systems such as thermites (i.e., Al + Fe_3O_4) or lesser known exothermically alloying compositions called Pyrofuze [2] (i.e., Pd + Al) also belong to the same class of reactions and were widely used in specialized pyrotechnic devices for more than half a century. These reactions typically propagate through

these compositions with flame speeds on the order of cm/s.

From a thermodynamic point of view, any of the gasless SHS reactions that generate high-temperature condensed products are suitable for use in heating elements for materials processing. In practice, however, some specific demands should be satisfied to make heat transfer from the SHS combustion products to the heated specimen effective. Thus, it is desirable that condensed combustion products be in a liquid state with the solidification temperature of the melt considerably lower than the flame temperature. The liquid state of the products during heating ensures a close contact between the products and the specimen container, eliminating any possible air gaps that might cause considerable resistance to the heat transfer. For solid products, these air gaps are difficult to avoid due to the difference in thermal expansion coefficients of various solids. In addition, the heat transfer coefficients are much higher in melts than in porous solids. It is also important to minimize initial porosity of the precursor mixture. Gases that are trapped in the pores or compacted loose powders of traditional SHS precursors expand during combustion, leading to formation of large volumes of gas bubbles inhibiting efficient heat transfer in the liquid combustion products.

A new type of SHS system recently developed at McGill University is based on highly energetic metal-sulfur combustion reactions that are able to satisfy these demands [3]. The unique properties of metal-sulfur reactions, which include very high flame temperatures, low ignition temperatures, liquid combustion products, nonporous charges, and gasless combustion make them ideally suited for the proposed heating application.

THERMODYNAMICS OF METAL-SULFUR COMBUSTION

Sulfur is situated directly below oxygen on the periodic table, and its properties as a reactant resemble many of the characteristics of oxygen. In particular, it reacts exothermally with many metals to form stable refractory compounds. However, unlike oxygen, sulfur is solid in its elemental form and can be premixed with fuel (metal) directly, whereas oxygen can only be used in a chemically bonded state, i.e. in the form of oxides, salts, etc. Thus, in spite of the considerably lower enthalpy of formation of sulfides in comparison to oxides, the energetic potential of metal-sulfur reacting compositions is comparable to or exceeds the energetic potential of the most powerful oxygen-based pyrotechnics, i.e. thermite (see Fig. 1).

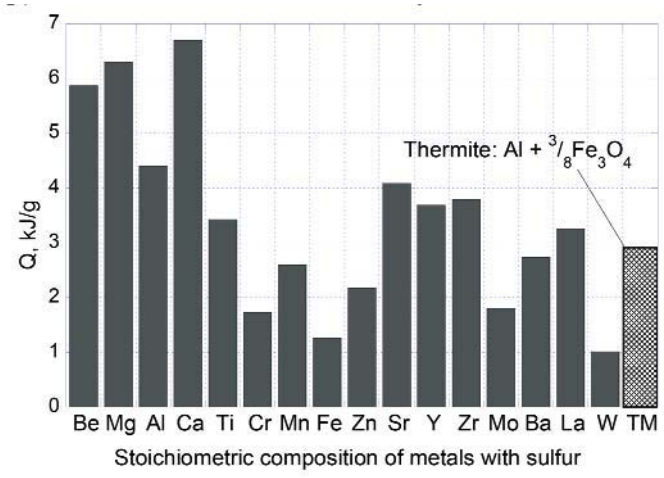

Figure 1 Heat productivity of different metal-sulfur reactions in comparison to common thermite reaction.

Most metal-sulfur reactions are sufficiently energetic to support self-sustained propagation of a combustion front if small metal particles are mixed with sulfur to provide a sufficiently large surface area for the reaction. Thermodynamic calculations also show (Fig. 2)[1] that in most cases adiabatic flame temperature of the metal-sulfur flame is much higher than the melting point of the corresponding sulfide product. Some metal-sulfur reactions also demonstrate equilibrium temperatures that are among the highest temperatures achieved with SHS and pyrotechnic compositions. For example, the adiabatic temperature of Ca-S and Ba-S reactions exceed 5000 K and adiabatic temperature of Mg-S, Al-S, Ti-S, and Zr-S combustion is close to 4000 K. Thermodynamic calculations also indicate that some of metal-sulfur reactions are practically gasless (Cr-S, Fe- S, Y-S) with equilibrium pressure of the combustion products well below atmospheric pressure at the adiabatic flame temperature. Several reactions, such as Ti-S, Mn-S, and Zr-S exhibit only moderate pressure (below 5 bar) of gaseous products in combination with flame temperatures that exceed 3000 K.

In order to prevent boiling and formation of gas bubbles inside liquid combustion products, combustion has to be performed at ambient pressure that is greater than calculated equilibrium gas pressure of constant volume combustion. For some of the most energetic compositions, equilibrium pressure can exceed several hundred bars, which might pose an unacceptable hazard for a number of practical applications. Using nonstoichiometric and ternary compositions can lower the operating pressure of the heating element. Thus, fuel-rich compositions can be used in mixtures where the metal has very high boiling point, as for example in the Ti-S reaction. If the reactive metal has a low boiling point, such as the Ca-S composition, the mixture can be diluted with the corresponding refractory metal sulfide. Alternatively, combination of the low gas-producing elements, such as Cr, with more energetic element, such as Mn, can be used to design ternary compositions that have the desired low gas pressure and, in the same time, a relatively high combustion temperature.

The thermodynamic analysis demonstrates that due to a large number of different combinations available, metal-sulfur combustion offers considerable flexibility in tailoring combustion thermodynamics to a wide variety of practical applications with

[1] The equilibrium thermodynamic analysis was performed with software package "Thermo" developed at the Institute of Structural Macrokinetics (Moscow) [4].

diverse demands on operating pressure and temperature.

PREPARATION AND COMBUSTION CHARCTERISTICS OF METAL-SULFUR SUSPENSIONS

The major deficiency of common SHS and pyrotechnic mixtures in heating applications is that they are loose or compacted powder mixtures that are difficult to form into complex shapes. Even when compacted under high pressure, these mixtures retain some residual porosity that often results in violent combustion due to the thermal expansion of the gases trapped in pores. The organic binders, which are usually used to reduce porosity in pyrotechnics and propellants, are unacceptable for proposed heating application as their decomposition and combustion produces large volumes of gas. Metal-sulfur combustible mixtures are a unique example of binary pyrotechnic and SHS compositions that can be formed in nonporous charges without the use of an additional binder. Because the melting point of sulfur (115 °C) is well below the ignition temperature of the mixture, the sulfur in the composition can be safely melted without initiating reaction, thus converting the powder mixture into a homogeneous liquid suspension free of gas bubbles. This suspension than can be easily molded and solidified in any shape, forming a hard, nonporous solid charge.

The solidified metal-sulfur suspension is moisture insensitive (sulfur is insoluble in water) and is not affected by air. It can be stored without any special protection for an indefinite period without degradation of its combustion properties. Unlike thermites that have very high ignition temperature (especially when compacted) and which usually require special ignition mixtures for their initiation, metal sulfur suspensions have ignition temperatures in the range of 300-500 °C [3] and are easy to ignite by common ignition sources (i.e., glowing wire). The flame propagation through gasless-combustion sulfur suspensions is smooth and nonviolent and demonstrates speeds in the range of 2-8 mm/sec, which is typical for many SHS and pyrotechnic compositions.

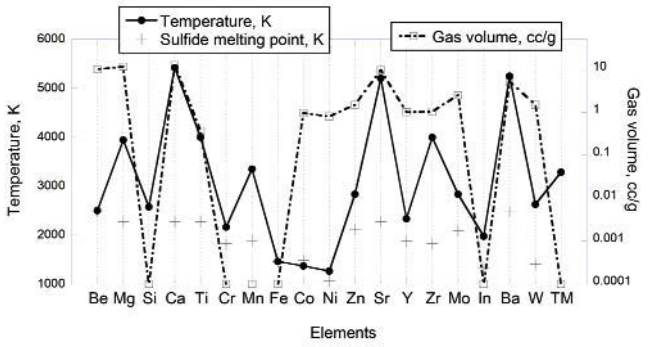

Figure 2 Equilibrium calculations of the adiabatic flame temperature and volume of gaseous products at 100 bar ambient pressure for the reaction of elemental metals with sulfur and the thermite reaction (TM). Short horizontal lines indicate melting points of corresponding sulfides.

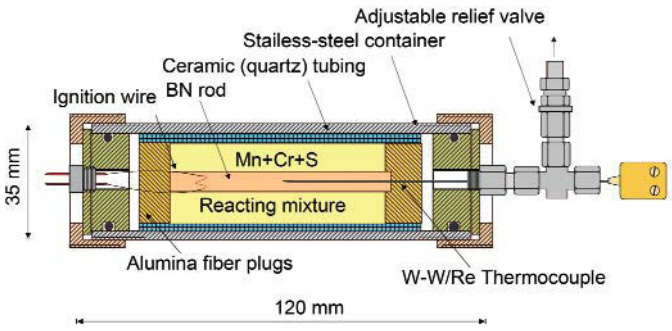

Figure 3 Schematic of the experimental combustion heating element.

Figure 4 Photograph of the heating assembly after combustion.

TESTING THE PROTOTYPES OF THE GASLESS COMBUSTION HEATING ELEMENT (GCHE)

To prove feasibility of the proposed gasless combustion-driven furnace concept, a laboratory prototype of the GCHE has been designed, built, and tested using Cr-S and ternary Mn-Cr-S mix-

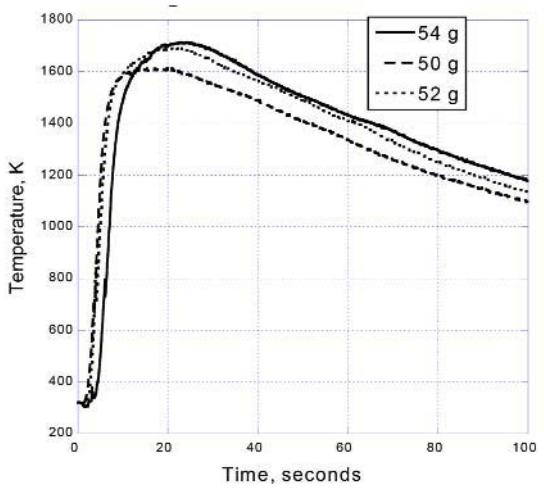

Figure 5 Time-temperature histories in the center of the boron nitride rod heated by the product of Cr-S combustion (note different weight of the charges).

tures, which demonstrate nearly gasless combustion at normal pressure.

The schematic of the experimental assembly that houses the combustion heating element is shown in Fig. 3. The element is hermetically sealed inside a stainless-steel tube by steel cups with Teflon o-rings. The combustible Cr-S or Cr-Mn-S mixture is cast inside a fused silica glass or ceramic tube and is covered at the ends by alumina fiber insulation plugs. A 0.1-mm thick electrically heated tungsten wire imbedded at the end of the charge provides ignition. A 6.5-mm diameter boron nitride rod in the center of the charge simulates the container with material sample inside. The rod is drilled to a half-length to accommodate fine-gauge W-W/Re thermocouple shielded inside thin tantalum tubing.

The photograph of the heating charge after combustion is shown in Fig. 4 and demonstrates that combustion only partially melted the quartz tube, otherwise causing no visible change in shape and dimensions of the assembly. Characteristic temperature traces registered by the thermocouple imbedded in the sample heated by Cr-S combustion products are shown in Fig. 5. As can be seen, the observed deviation in time-temperature history in different trials is relatively small and correlates with variation in weight of reactive mixture in different experiments.

The dependence of the measured peak sample temperature on the composition of the reacting Cr-Mn-S suspension is shown in Fig. 6. As can be seen, the temperature difference between calculated adiabatic temperature of combustion products and the measured sample peak temperature increases with the increase of the flame temperature (i.e., is larger for mixtures with higher Mn content), which is probably the result of the increasing role of the radiation component of heat loss at high temperatures.

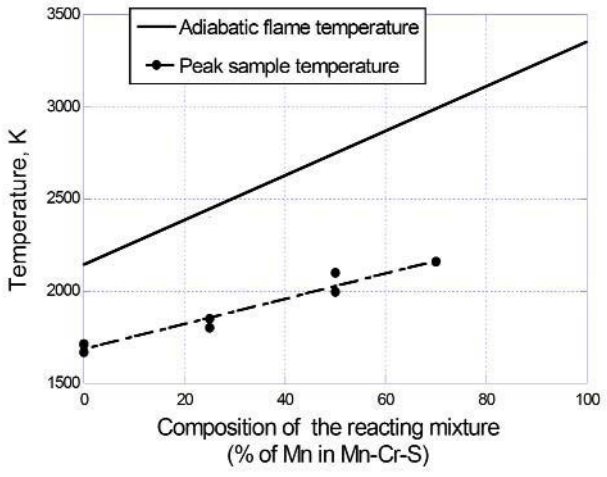

Figure 6 Calculated adiabatic temperature of Mn-Cr-S combustion and measured sample peak temperature as a function of mixture composition.

GASLESS COMBUSTION HEATING ELEMENTS VAPOR DEPOSITION EXPERIMENTS

Besides high energy density and gasless combustion, metal-sulfur heating suspensions have another important asset that may considerably expand the field of their application. The density of sulfides is higher than the density of the metal-sulfur precursor charge (for example, the density of Mn-S, solidified stoichiometric suspension is about 3.57 g/cc and the density of the solidified combustion product, i.e. MnS is about 3.99 g/cc). Thus, in spite of having been heated to very high temperatures, combustion products occupy a somewhat smaller volume than their precursor reactants. As a result, hermetically sealed enclosures that are completely filled with reacting metal-sulfur suspension are not significantly stressed and do not deform during the combustion process. As an example, the photograph on Fig. 7 shows combustion inside stainless steel tube filled entirely with liquid reactive suspension. After combustion, when the tube has cooled down to the room temperature, it exhibits no residual deformation.

The hermetically confined metal-sulfur combustion (gasless flame in tube) is utilized in the design of a Physical Vapor Deposition cell for microgravity experiments on board parabolic flight aircraft (these experiments are in preparation by the Thin Films and Photonics Research Group at Moncton University under Canadian Space Agency support). The experi-

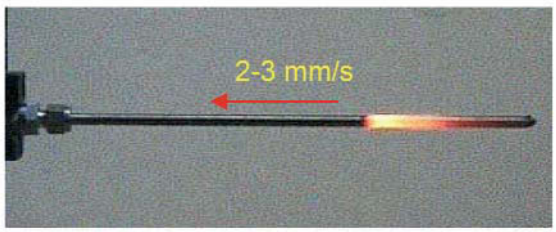

Figure 7 Photograph of the hermetically sealed tube heated from inside by Mn-S combustion.

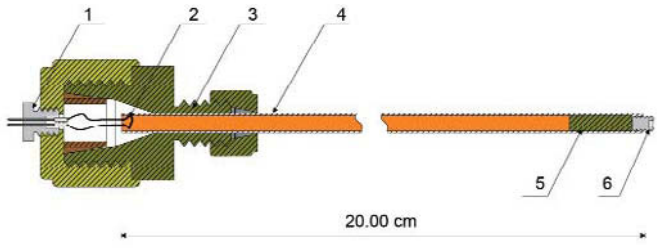

Figure 8 Practical design of the Traveling Flame Heating Element (TFHE) with electrical ignition system. 1–glass-to-metal sealed feed-through two-pin connector, 2–tungsten ignition bridge wire, 3–reducing union 4–6.3 mm OD SS tube with reacting mixture, 5–brass rod, 6–set screw sealed with high temperature pipe sealant.

mental PVD cell employs a gasless combustion heating element placed in the middle of the vacuum-sealed rectangular chamber divided into three isolated sections by thin copper baffles. The heating element (stainless-steel tube filed with metal-sulfur suspension) is insulated at both ends by higher-pressure fittings and has a tungsten ignition wire imbedded into reactive mixture at one end. The design of the hermetically sealed traveling-flame heating element is shown in Fig. 8.

The evaporating material is deposited directly onto the surface of the flame tube or, when lower deposition temperature is required, onto the surface of a cylindrical copper sleeve surrounding the tube. The reactive mixture is ignited during the accelerating phase of the airplane parabolic trajectory (1.8-2 g). The flame that propagates with constant speed of about 2-3 mm/s will reach the middle section of the cell during reduced gravity part of the parabolic trajectory. It will move into the third section of the cell during pull-up maneuver of the aircraft when the gravity level again exceeds 1.8 g. Thus, by using traveling heat source formed by the propagating flame, material evaporation can be performed at elevated and reduced gravity conditions within the same cell.

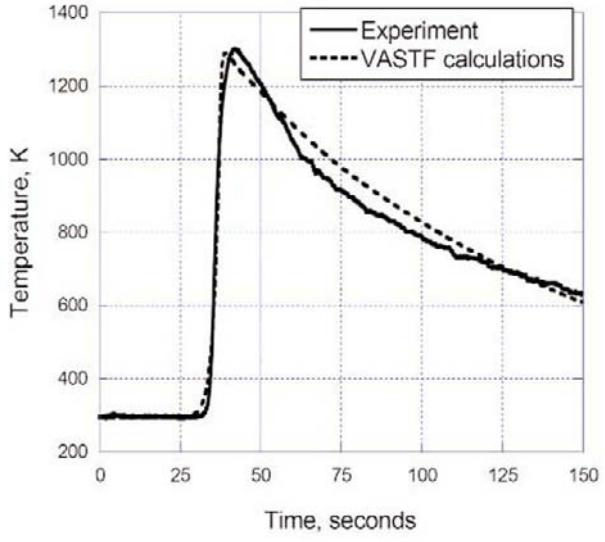

Figure 9 Experimental and calculated time-temperature histories of the tube surface.

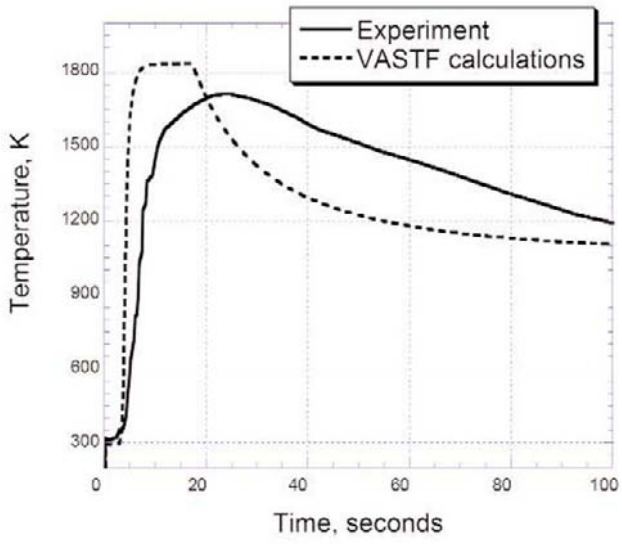

Figure 10 Experimental and calculated time-temperature histories in the center of heating arrangement shown in Fig. 3.

NUMERICAL MODELING OF GASLESS COMBUSTION HEATING ELEMENTS

In parallel with experimental development of the combustion heating elements, a numerical code that allows accurate description of the combustion heating process has been developed. After extensive verification and validation using the experimental results, this code is expected to be a valuable tool in the design of different heating schemes allowing their verification and analysis without extensive and expensive experimental work.

Numerical modeling of the heat transfer process in a gasless combustion heating elements requires solution of a complicated moving boundary problem involving propagating combustion front, convection and continuous solidification of cooling combustion products. Numerical simulations were performed through modification of a finite-element heat-transfer program, named VASTF [5], which was developed by Martec LTD over the past three decades. An algorithm, using the concept of a prescribed initial temperature, was used to describe combustion front propagation in the reacting matrix. A phase change modeling capability was developed to model phase changes in both combustion products and the heating sample. Among the proposed finite element formulations for phase change problems, the method, which converts the phase change problem into an equivalent problem with temperature-dependent heat capacity [6, 7], was found to be the most compatible with the VASTF general-purpose finite element program. To enhance the reliability of numerical computations, smoothed finite difference formulations were used to approximate the temperature derivatives involved in the calculations of equivalent heat capacity at each numerical integration point [7]. The example of the numerically predicted time-temperature history of the traveling flame heating element described in the previous section is shown in Fig. 9 and Fig. 10 demonstrates comparison of calculated and computed time-temperature histories in the center of the heating element in Fig. 3. The observed larger disagreement in the later case is probably because the combustion front in this essentially three-dimensional situation was modeled by a flat surface propagating from the ignition point with constant speed, however experimental observation shows that this is rarely the case in reality [3].

CONCLUSION

The use of highly energetic, gasless reactions permits a novel approach to heating elements for materials research in microgravity to be realized. In particular, the use of metal-sulfur heating compositions (with high flame temperatures, liquid products of combustion, minimal gas production at modest pressure, and easily prepared, nonporous charges) permits the concept of using gases combustion as a heating source to be implemented for a variety of desired experimental conditions. A prototype furnace capable of heating representative materials sample to 2300 K at a rate of 200 °C/sec has been demonstrated. A second prototype, designed specifically to exploit the moving heat source of the propagating flame front in order to perform physical vapor deposition during variable gravity experiments, has also been tested. A numerical model of these devices has shown good agreement with the experimentally measured temperature profiles, providing a computation tool for the further design and optimization of the gasless combustion heating element concept.

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