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Consolidated Al/Cu_2O Thermites

L. D. Haws, M. D. Kelly and J. H. Mohler

September 28, 1978

Monsanto

MOUND FACILITY
Miamisburg, Ohio 45342

operated by
MONSANTO RESEARCH CORPORATION
a subsidiary of Monsanto Company

for the
U. S. DEPARTMENT OF ENERGY

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Foreword

The material in this topical report originally comprised an oral presentation at the Sixth International Pyrotechnic Seminar (Estes Park, Colorado, July 17-21, 1978), but did not appear in the proceedings of that meeting.

Part II, a sequel to this material with A. Latkin of Lawrence Livermore Laboratory as an additional author, was published in the Proceedings of the Sixth International Pyrotechnic Seminar.

Abstract

Processes were developed at Mound Facility to produce high density Al/Cu_2O thermite composites. Consolidation of the precursor thermite powders produces efficient chemical heat sources that are safe to handle, are machineable, and generate minimum gas pressure upon reaction. This paper describes some of the ignition characteristics and performance features of selected consolidated thermite systems. In addition, an inexpensive low energy input system for igniting consolidated thermites is described.

Introduction

Chemical reactions occurring according to the equation:

$$MO_{(s)} + M'_{(s)} = M'O_{(s)} + M_{(s)} + \text{Heat} \qquad (1)$$

are generally referred to as thermitic reactions. Starting materials are an intimate mechanical mixture of a powdered active metal (M') whose oxide possesses a high heat of formation and a metal oxide (MO) of much lower heat of formation that is easily reduced. Aluminum is often used as the reducing metal; in this case the reaction is sometimes called aluminothermic. In most applications of aluminothermic reactions the primary interest is a large thermal output in a short period of time. As shown in Table 1 aluminum in combination with metal oxides having a low heat of formation can provide a wide range of thermal outputs on both a weight and volume basis.

Table 1

THERMITIC COMBINATION OF ALUMINUM WITH SELECTED METAL OXIDES

Metal Oxide	Thermal Output (kcal/g)	Thermal Output ($kcal/cm^3$)
MnO_2	1.15	4.6
MoO_3	1.10	4.2
CuO	0.98	5.0
Fe_2O_3	0.95	4.0
Fe_3O_4	0.87	3.7
PbO_2	0.73	5.1
Cr_2O_3	0.63	2.6
WO_3	0.69	3.8
Cu_2O	0.58	3.1
Pb_3O_4	0.47	3.5

We at Mound Facility are currently interested in the Al/Cu_2O system producing the aluminothermic reaction:

$$2Al + 3Cu_2O \longrightarrow Al_2O_3 + 6Cu + 580 \text{ cal/g} \quad (2)$$

Of special interest is the development of safe chemical heat sources that can be produced in a variety of geometries and that produce minimum gas pressure on reaction.

Equations (1) and (2) above suggest gasless reactions. In actuality some gas pressures are developed as a result of:

1. Transient species (e.g., Al_2O and AlO) occurring at the high reaction temperatures,

2. Impurities in and/or adsorbed species on the metal and/or metal oxide particles, and

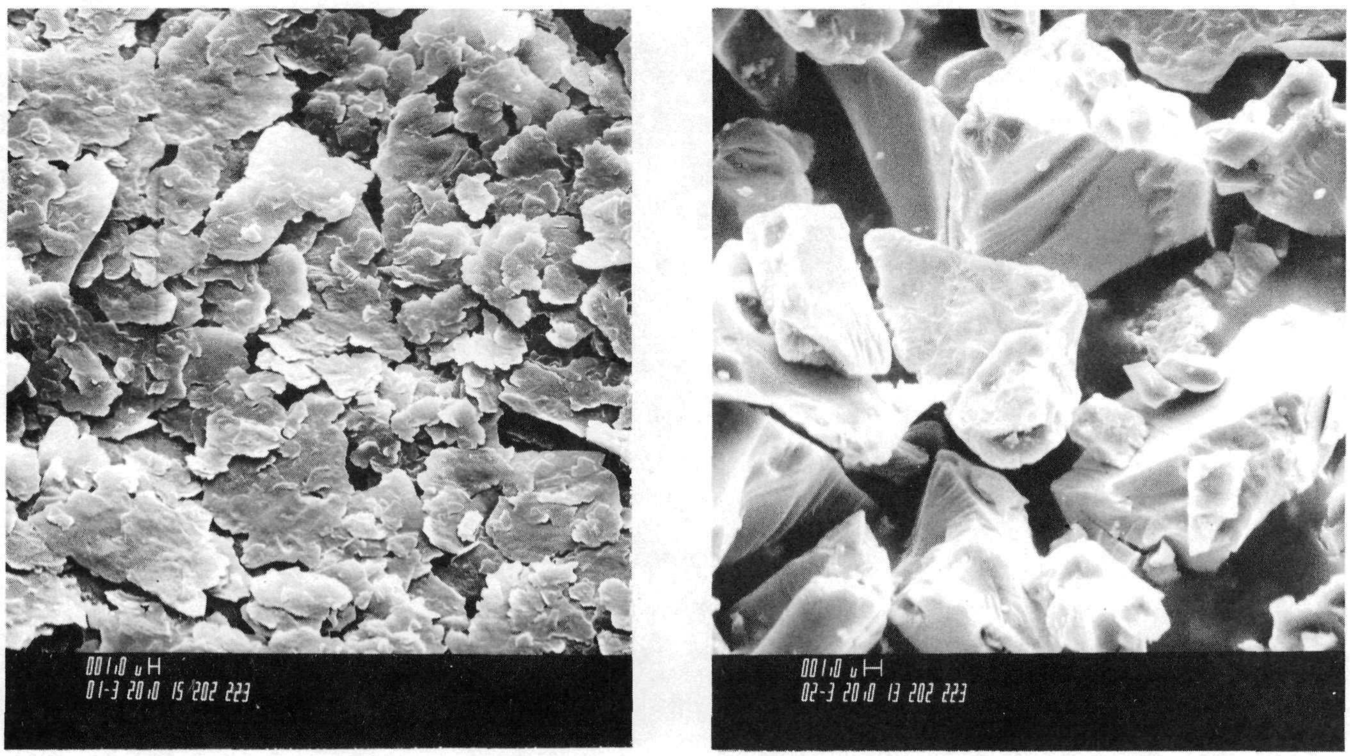
3. Expansion at the reaction temperature of interstitial gases (e.g., air) in the thermite mixture.

Of the three causative factors listed above the third is most readily controlled, at least in principle, by elimination of void volume. We at Mound Facility have developed a process for consolidating mixtures (without binding agents) of aluminum and copper oxide powders close to maximum density. The resultant product is a mechanically strong thermite compact that is safe to handle but is relatively easy to ignite and is machineable to achieve a variety of geometries.

Process

Thermite Powder Mixing

Reynolds XD28 flake aluminum and Cerac "Pure" cuprous oxide powders were used to prepare theoretically stoichiometric mixtures (11 wt % Al and 89 wt % Cu_2O). Scanning Electron Photomicrographs of powders typically employed are presented in Figure 1. In some development work spheroidal aluminum or a eutectic aluminum-silicon alloy powder was employed; performance attributes of the consolidated thermites containing these substitutes are described below. Cuprous oxide was initially sieved through a 400-mesh screen to remove oversized particles; aluminum powders were used as received. Dry mixing for one hour in a V-blender provided adequate homogeneity of the composite thermite powder.



Flake aluminum   Cuprous oxide

FIGURE 1 - Scanning electron photomicrographs illustrate fuel and oxidizer particle sizes and shapes.

Consolidation Procedure

Consolidation of the Al/Cu_2O thermite powder was done in preheated, highly polished, POCO graphite dies (Figure 2) under a blanket of dry nitrogen. This atmosphere alleviates oxidation of the graphite, thereby extending die life. Consolidation conditions (selected from a parametric study) routinely employed to obtain high-strength compacts at nominally 90% (87.9 $\pm$ 1.3%) maximum density were:

Temperature:	480°C
Pressure:	10,000 psi
Dwell time:	1 hour

These conditions are adequate to plastically deform the aluminum and to produce a solid compact consisting of Cu_2O particles in an essential continuum of aluminum (Figure 3). The mechanical

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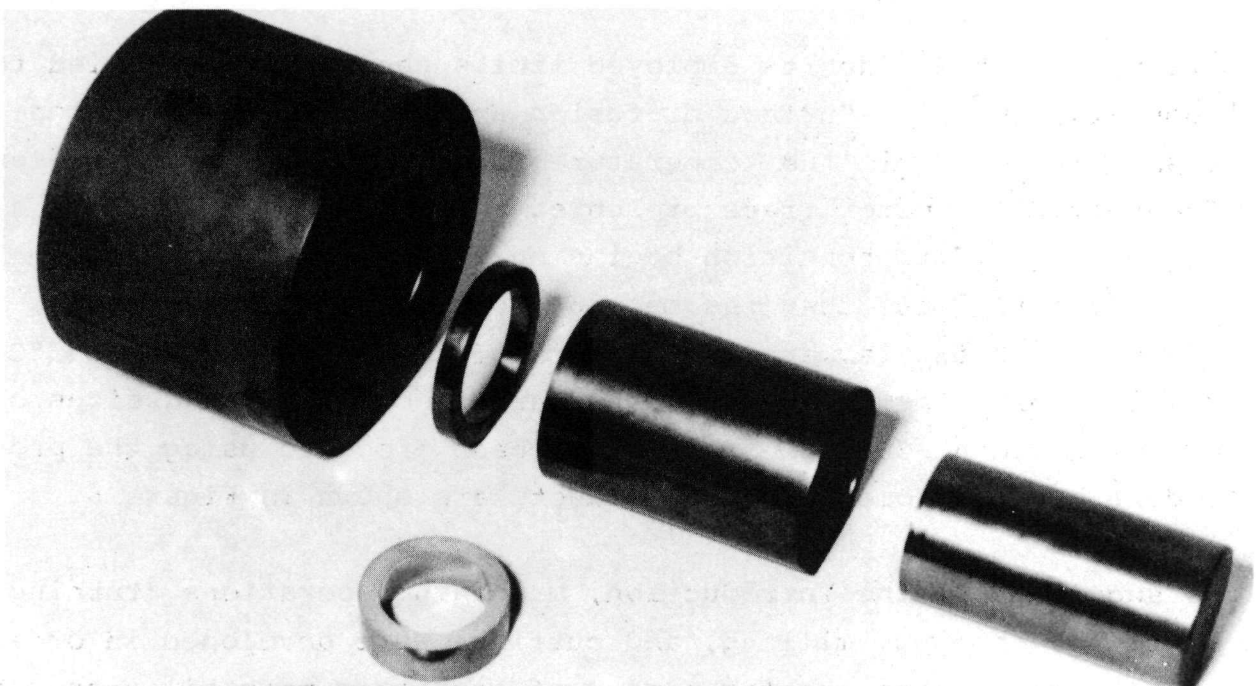

FIGURE 2 - Current consolidation involves hot-pressing of thermite powder in high strength self-lubricating graphite dies.

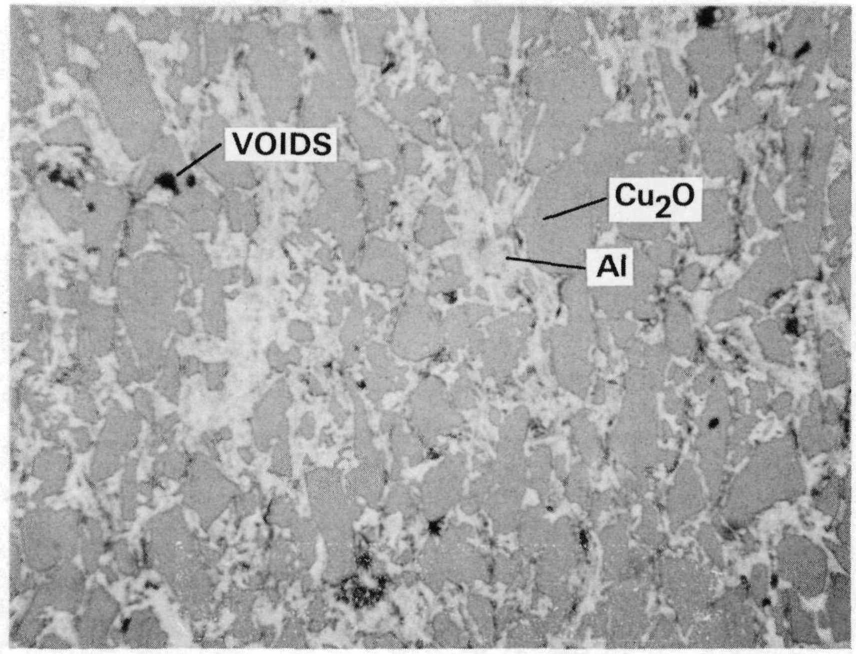

FIGURE 3 - Hot pressing of flake-aluminum/cuprous oxide powders produces a high density compact of oxide embedded in an essential metallic continuum.

strength of the graphite employed limits the pressure applied to about 10,000 psi. Surface diffusion and pre-ignition reaction possibilities limit the temperature to about 480°C; the Differential Scanning Calorimeter trace presented in Figure 4 demonstrates a highly exothermic condition beginning at slightly above 500°C--significantly less than the melting point of aluminum (660°C), but at about the Tammann temperature of Cu_2O (based on a 1235°C melting point for that oxide). A variety of shapes and sizes of consolidated Al/Cu_2O thermites have been produced using the procedure above. Some of these products are shown in Figure 5.

As suggested in the Introduction, machining operations (turning, drilling, tapping, milling, and cutting) were developed in order to produce an even greater number of geometric possibilities. An example of a piece of Al/Cu_2O thermite machined from a consolidated ring is shown in Figure 6. Sharp, high-speed steel tool bits are used for turning. Maximum surface speed of the work piece is 1000 in./min with a maximum feed rate of 0.5 in./min. For milling and drilling, a tool speed of 770 rpm is recommended with a four-flute

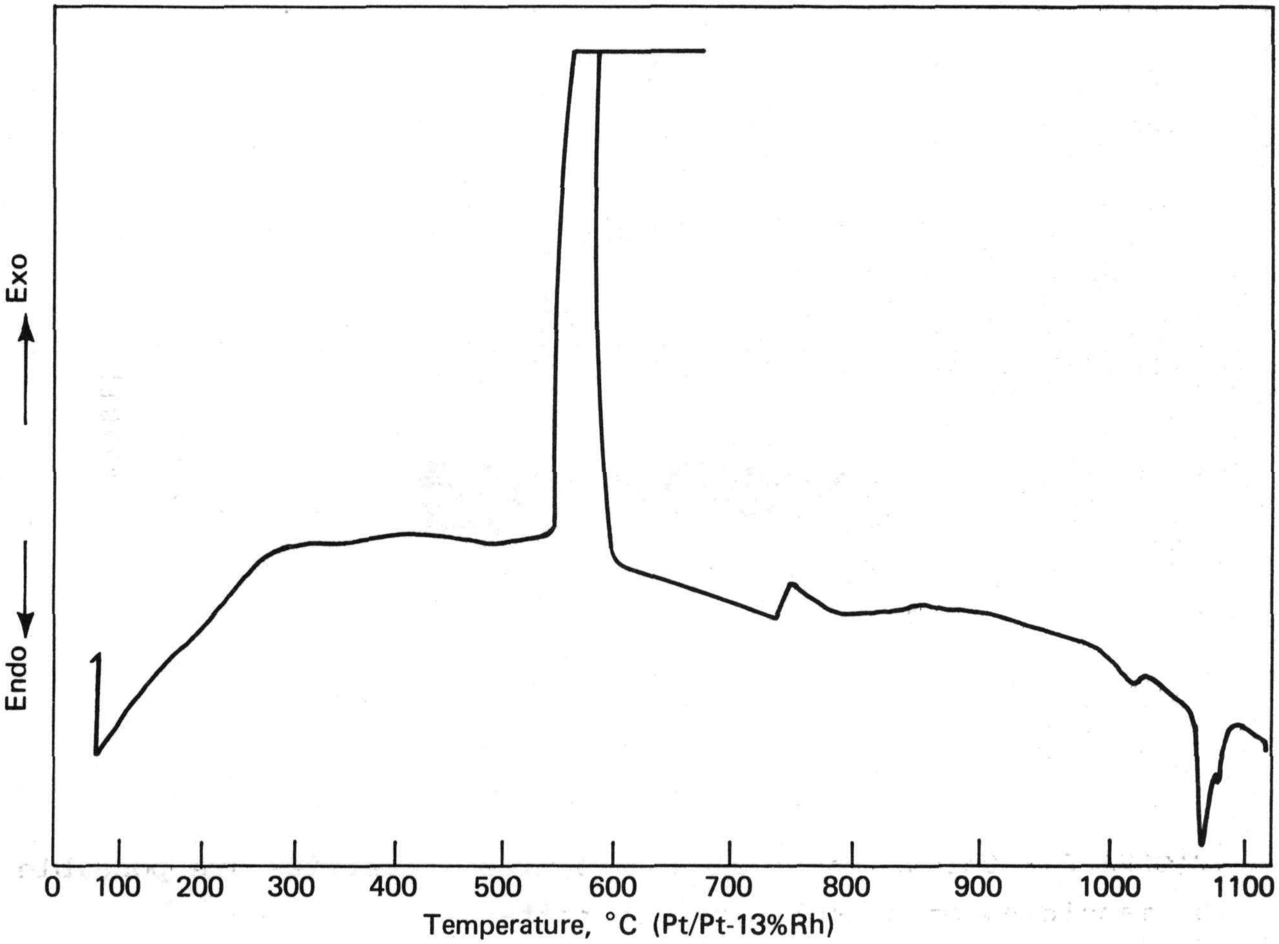

FIGURE 4 - A DSC trace of consolidated Al/Cu_2O illustrates a large exotherm slightly above 500°C.

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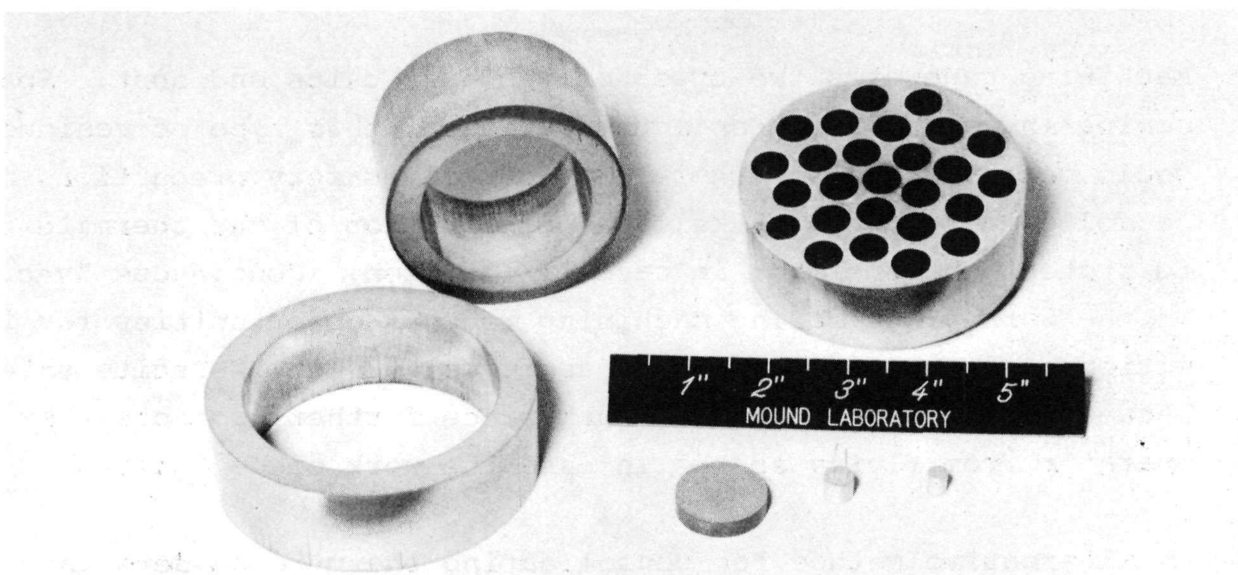

FIGURE 5 - A variety of thermite geometries and sizes can be produced by hot pressing.

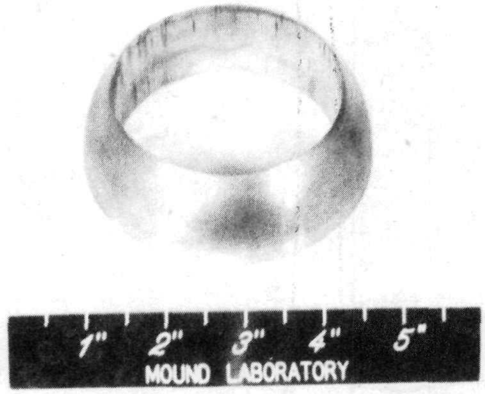

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FIGURE 6 - Unique chemical heat source geometries are possible by machining of consolidated thermites.

end mill. Tapping requires a long lead tap and as slow a rate as possible. No lubrication is used with any machining operations.

Machining generates two types of residue, chips and dust. Sparks coming in contact with an accumulation of this type of residue could cause ignition. Therefore, certain safety precautions must be followed to reduce likelihood of ignition of the thermite chips or to protect the operator in case of ignition. Continuous "vacuuming" of the work piece during machining reduces opportunities for ignition by removing the residue as it is formed. A Lucite shield between the operator and the work piece further protects the operator from flying sparks in case the work piece ignites.

An alternative method for consolidating thermite powders involves Hot Isostatic Pressing (HIP). Some preliminary development work was done for us with this process by Battelle Columbus Laboratories. By this process Al/Cu_2O thermite pellets of 100% TMD (theoretical maximum density) have been produced. With such pellets, reaction is more uniform. The HIP process also facilitates production of larger and more complex geometries.

Characteristics of consolidated Al/Cu_2O thermites

Burn Rates

The linear burn rate of consolidated Al/Cu_2O thermite products was measured using an optical fiber method developed at Mound Facility for other pyrotechnic and explosive materials [1]. In this method, two or more fibers are located in cylindrical metal container walls at different distances from the point of ignition. When the reaction reaches each fiber, light from the reaction is transmitted to separate detectors. A record is made of the detector responses on separate but simultaneously triggered inputs to a Biomation 8100 Transient Pulse Recorder. From the fiber locations and the time difference between detector responses, a linear velocity can be calculated. Nominal burn rates are about 10 cm/sec for Al/Cu_2O consolidated to 75% of theoretical maximum density. Results to date suggest that the linear burn rate may be inversely related to density. Burn rates evaluated from high speed cinephotographs (3,500 frames/sec) confirm the order of magnitude for burn rates.

Calorific Output

Calorific output was determined for consolidated Al/Cu_2O thermites ranging in composition from 50 to 93 wt % Cu_2O. Mixtures were consolidated using slight variations to the conditions cited above. The resulting pellets were fired in a 100-cm^3 bomb under 30 atm of argon. Ignition was accomplished by embedding a short piece of pyrofuze braid (0.0172 g, 32 cal/g) in each pellet during pressing. Calorific yields obtained are shown in Figure 7.

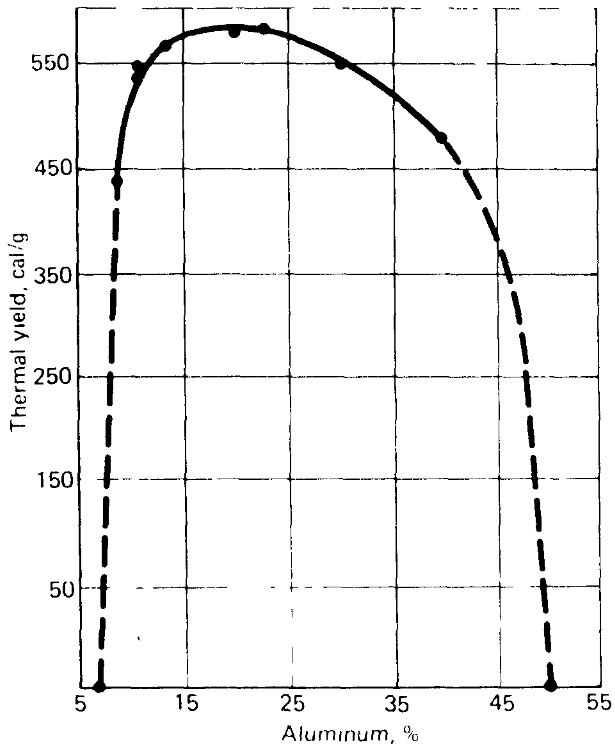

FIGURE 7 - The relationship between composition and thermal output for the Al/Cu_2O thermite system.

According to Equation (2) the theoretical maximum of 580 cal/g should be observed for the mixture consisting of 11 wt % Al and 89 wt % Cu_2O. Although this maximum was not obtained for any composition, the experimental results shown here suggest that a fuel-rich composition containing 20 wt % Al is actually the most efficient. A mixture rich in Al can also be expected to produce consolidated thermite pellets with improved mechanical properties although this has not yet been evaluated.

Zero-Volume Pressure Measurement

A graphite test assembly was fabricated to measure the pressure rise that results from the reaction of consolidated Al/Cu_2O thermite in a zero volume condition. A sketch of the assembly is shown in Figure 8. For this measurement, the thermite charge is hot pressed directly in the apparatus; therefore, no free volume

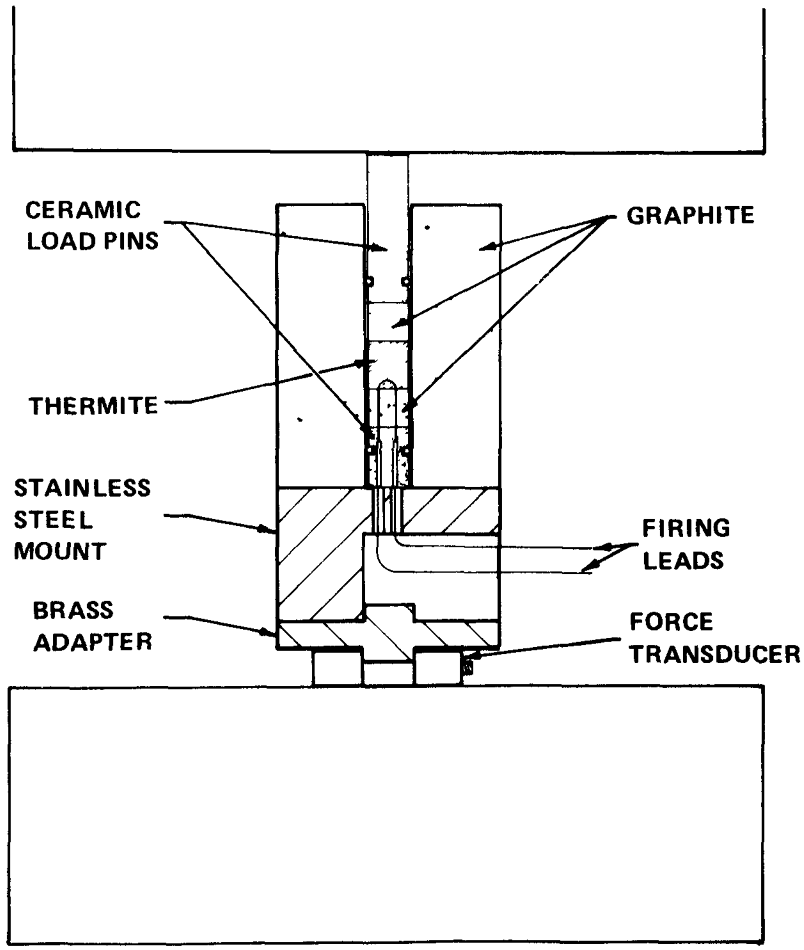

FIGURE 8 - Zero-free volume pressure test assembly.

is left to trap gas. After pressing, the O-rings are installed and the complete assembly is placed in a hydraulic press. The press is closed until a small force is registered by the transducer. After the charge amplifier is zeroed, the thermite is ignited. Force resulting from charge expansion is detected by the transducer and recorded on a Biomation Transient Recorder. A pressure record for a pellet having a density 70% of theoretical maximum is shown in Figure 9. Peak and final pressures were 217 and 80 psi, respectively, considerably lower than more conventional pyrotechnic systems.

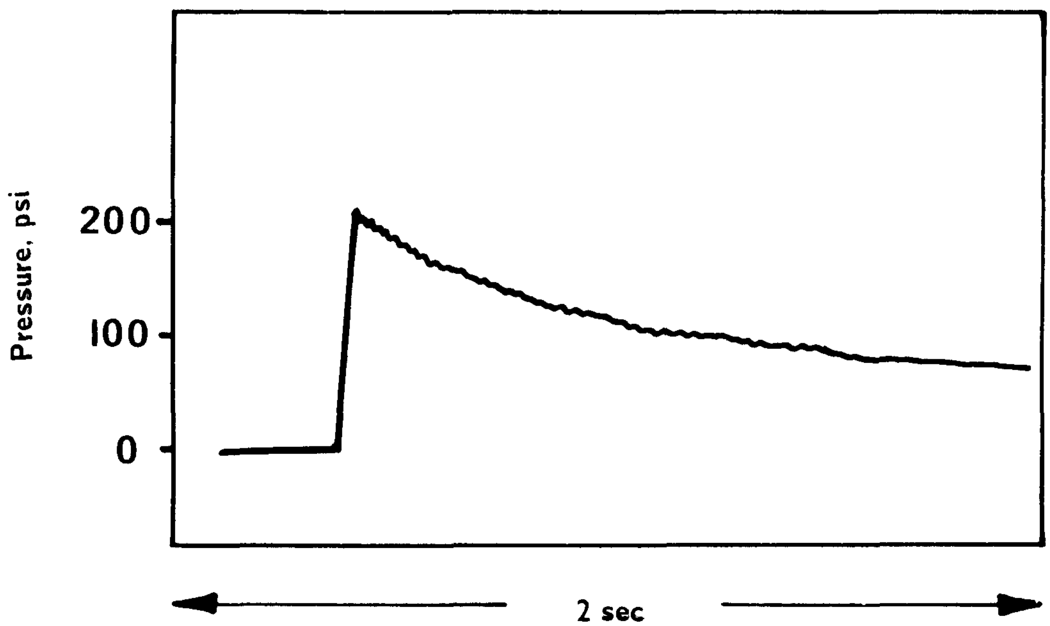

FIGURE 9 - Typical pressure-time record of consolidated Al/Cu_2O reaction in zero free-volume test assembly.

Mechanical Strength

The tensile strength of Al/Cu_2O thermite (11/89 wt %) consolidated to various densities was determined from diametral compressive strength measurements. The relationship can be expressed by the following equation:

$$\sigma = \sigma_o \, e^{-b\varepsilon} \qquad (3)$$

where σ = tensile strength, psi

σ_o = tensile strength at the theoretical maximum density (5.29 g/cm^3), psi

ε = fraction porosity, and

b = an experimentally determined constant.

It was found that σ_o = 5855 psi and b = 4.95.

Compressive strength was also measured for samples having varying densities between 75 and 100% TMD. A linear relationship was evident over the range of measurement and is expressed by the equation:

$$s = 1.82 \times 10^5(1-\varepsilon) - 1.234 \times 10^5 \quad (4)$$

where s and ε are compressive strength and porosity, respectively.

Formulation variations

The product/process descriptions above dealt exclusively with consolidation of cuprous oxide powder with aluminum flakes. We have also conducted some studies with spheroidal aluminum powders as well. The result of substituting spheroidal for flaked aluminum is a matrix consisting of aluminum particles embedded in an essential continuum of copper oxide. As expected both the electrical and thermal conductivities are significantly reduced with this type of compact.

In order to facilitate ignition of large masses of consolidated Al/Cu_2O thermite systems, we found it advantageous to start with a more sensitive (less energy for ignition) composition, specifically AlSi/Cu_2O. The aluminum-silicon alloy powder is the eutectic composition, which lowers the melting point of the fuel in the thermite from 660°C to 577°C. Furthermore, the AlSi particles are spherical as opposed to the flake shape of the aluminum. This spherical AlSi fuel produces a discontinuous (therefore nonconductive) metallic phase in the thermite composite. The loosening of the aluminum lattice, with the attendant lowering of the melting point and the lower thermal/electrical conductivities, increases ignition sensitivity and provides a more reliable and more rapid burning reaction layer when the AlSi fuel is consolidated with Cu_2O on top of a flaked aluminum/cuprous oxide layer. This application is briefly discussed in the next section.

Thermite ignition system

Large masses of consolidated thermites are ignited most effectively with another smaller thermite pellet in which a piece of pyrofuze is embedded. A sketch of the furnace and die arrangement for producing igniter pellets is shown in Figure 10. Because the consolidated thermite is machineable, the igniter pellet can be inserted in a hole drilled in the more massive thermite composite.

The most efficient igniter pellet is actually a two-layer composite, but consolidated in a single operation, and consisting of two thermite compositions, specifically $AlSi/Cu_2O$ and Al/Cu_2O. Pyrofuze wire is embedded in a thin layer of the $AlSi/Cu_2O$ (still 11/89 parts by weight) composition. The remainder of the two-layer igniter pellet consists of the "standard" Al/Cu_2O composition; the latter slows down the burn rate with reduced splatter and facilitates ignition of the massive thermite geometry.

The igniter pellet is normally pressed at 425°C rather than 480°C because at the latter temperature diffusion can occur between the palladium-ruthenium in the pyrofuze and the aluminum in the pellet or the wire.

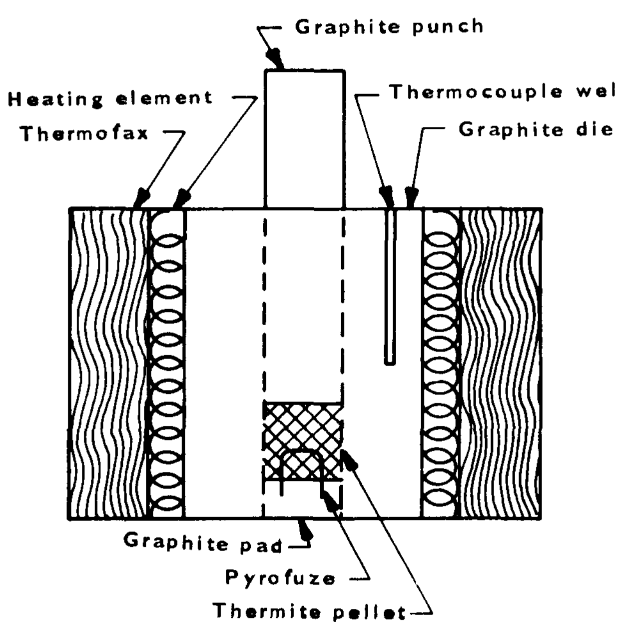

FIGURE 10 - Thermite igniter pellets are produced by embedding pyrofuze wire into the powder prior to hot-pressing.

The most reliable ignition system for massive consolidated thermites uses pairs of igniter pellets connected in parallel. Each pellet in the pair has an equal probability of ignition and should be sufficient to ignite thermite parts. Locating the two igniters close together in pairs amplifies the total output, producing a higher temperature in the main charge and enhancing ignition reliability.

Conclusions

Consolidation of Al/Cu_2O powders by hot pressing techniques produces solid composites that are useful as one-time chemical heat sources where the following characteristics are desired:

1. Thermal output approaching 580 cal/g
2. Safe-to-handle reactive solid.
3. Material with good mechanical strength.
4. Machineable thermite.
5. Essentially gasless reaction.

Reference

1. J. H. Mohler, W. J. Moodie, L. D. Haws and G. F. Hall, "Performance Characterization of High Explosives by Observing Growth to Detonation," in Combustion and Flame, Vol 32, pp. 285-294 (1978).

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