Aluminum Burn Rate Modifiers Based on Reactive Nanocomposite Powders

Demitrios Stamatis, Xianjin Jiang, Ervin Beloni, Edward L. Dreizin

Abstract

Aluminum powders have long been used in reactive materials for such applications as propellants, pyrotechnics and explosives. Aluminum has a high enthalpy of combustion but relatively low combustion rate. Addition of reactive nanocomposites can increase the burn rate of aluminum and thus the overall reaction rate. Replacing a small fraction of the fuel by a nanocomposite material can enhance the reaction rate with little change to the thermodynamic performance of the energetic formulation. This research showed the feasibility of the above concept using nanocomposite powders prepared by Arrested Reactive Milling (ARM), a scalable “top-down” technique for manufacturing reactive nanocomposite materials. The nanocomposite materials used in this study were 2B+Ti, and Al-rich 8Al+3CuO, and 8Al+MoO_3. The reactive nanocomposites were added to micron sized aluminum powder and the mixture was burned in a constant volume chamber. The combustion atmosphere was varied using oxygen, nitrogen, and methane. The resulting pressure traces were recorded and processed to compare different types and amounts of modifiers.

Introduction

Various nanocomposite materials are currently under development as potential components of different energetic formulations, from propellants to explosives, to pyrotechnics, e.g., [1 – 14]. The advantages anticipated from such materials are primarily due to a very developed reactive surface that facilitates a rapid initiation of the exothermic reaction and results in a nearly adiabatic reaction temperature. At the same time, the overall energy outputs from many exothermic reactions employed in such materials, including thermites, intermetallic, and metal-metalloid compositions, are smaller than the benchmark values for aluminum combustion in air or in other practically important oxidizers (e.g., ammonium perchlorate). Thus, replacement of aluminum as a fuel in most metallized energetic formulations with almost any of the nanocomposite materials currently under development would result in an overall reduction of the theoretical reaction enthalpy. This negative effect may be offset by an increase in the efficiency of metal combustion, so that the overall increase in practical performance is still anticipated. Therefore, the optimized composition would combine the high energetic output with the accelerated reaction rate. The approach discussed in this paper suggests that replacing a fraction of aluminum fuel with a reactive nanocomposite material could result in an acceleration of the ignition kinetics for all metal fuel. Aluminum particles located in vicinity of the igniting reactive nanocomposite particles would be heated more efficiently and ignite sooner. It is anticipated that a relatively small addition of the reactive nanocomposite material would provide a number of localized hot spots distributed in the igniting energetic formulation, which would accelerate ignition of the nearby aluminum particles, which, in turn, will accelerate ignition of their own neighbors. Effectively, the nanocomposite material will serve as a burn rate modifier for an aluminized energetic formulation. The amount of such modifier is expected to be a function of the specific formulation. In this paper, the proposed concept is initially explored for aluminum particles burning in a gaseous oxidizer in presence of products of hydrocarbon combustion. Such environments are relevant for both enhanced blast explosives and metallized solid propellants.

Materials

Reactive nanocomposite powders were prepared by arrested reactive milling (ARM), a high-energy mechanical milling technique [8 – 14]. Samples of three micron-sized, fully dense nanocomposite powders of 2B+Ti, 8Al+3CuO, and 8Al+MoO_3 were produced using a Retsch 400 PM planetary mill. Further details on the material synthesis are available elsewhere [13, 14]. Typically, the nanocomposite materials consist of micron-sized particles whereas each particle is a fully-dense, three-dimensional composite with characteristic dimension of material mixing of about 100 nm. Commonly, the morphology of composite is that of inclusions of one component, e.g., B, CuO, or MoO_3, embedded into a matrix of another component such as Ti or Al. In this study, the nanocomposite materials prepared by ARM were added to a spherical aluminum powder, 10 – 14 µm nominal particle size by Alfa Aesar. The mixing of aluminum and nanocomposite powders was performed using a SPEX Certiprep 8000 shaker mill operated without milling balls for three minutes. The particle size distributions for all powders used in this project were measured using a Coulter LS 230 Enhanced Laser Diffraction particle size analyzer. The size distributions and respective volume mean particle sizes for all powders are shown in Figure 1.

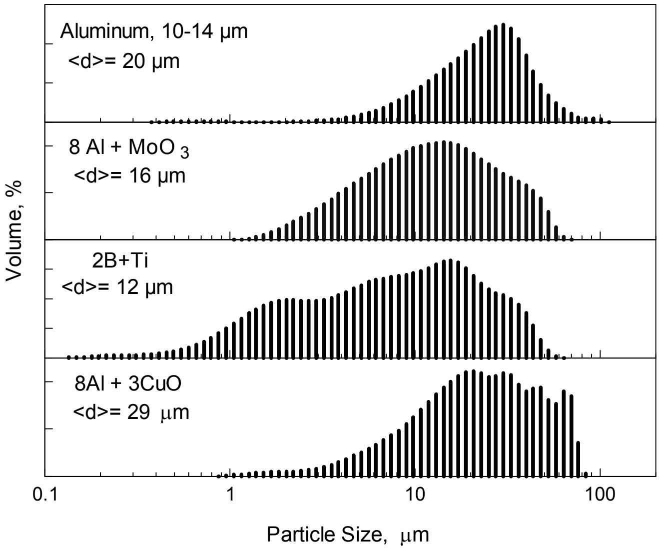

Figure 1 Particle size distributions for the different powders used in this project

Experimental

Constant Volume Explosion (CVE) experiments were performed with a set of materials including aluminum and aluminum mixed with different amounts of added nanocomposite burn rate modifiers. The details of the CVE experimental methodology and setup are described elsewhere [15 – 17]. Fig. 2 shows a simplified drawing of the CVE apparatus.

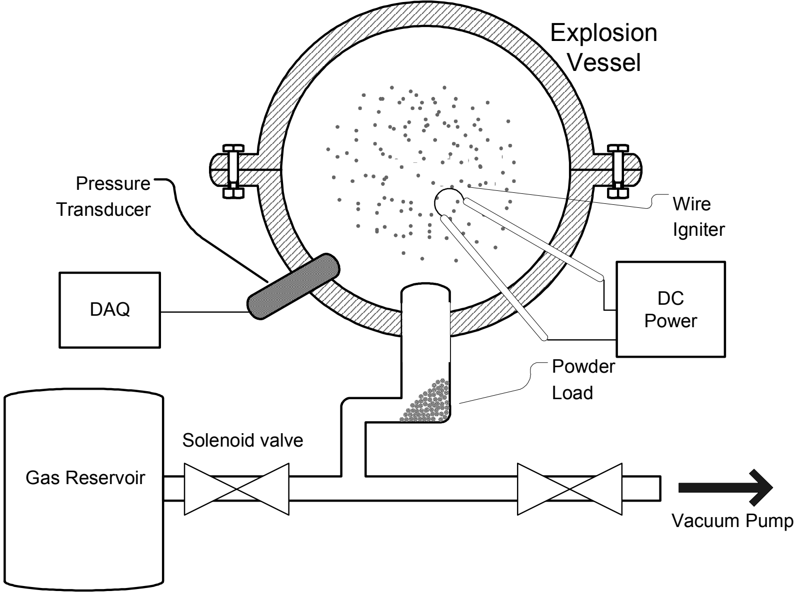

Figure 2 Drawing of constant volume explosion apparatus

In one set of experiments, the oxidizing environment was fixed to nominally include 3% CH_4, 21% O_2, and 76% N_2. The amounts of the nanocomposite powders added to aluminum were 10, 20, and 30 mass %.

The gaseous combustion products include moisture and carbon oxides, imitating the environment in actual propellants better than the previous CVE experiments performed in air [15, 16]. The powders were introduced into a nearly spherical 9.2 l vessel as an aerosol and ignited at the center of the vessel. The powder load was selected based on thermodynamic equilibrium calculations considering combustion of aluminum in the described above gas mixture. It was predicted that the maximum adiabatic flame temperature for the 9.2 l vessel occurs at an aluminum load of 2.64 g. Respectively, all experiments were performed with 2.64 g of powder loaded. Before the powder was introduced to the vessel, it was evacuated to less than 1 torr. The vessel then was filled with the 171 torr of O_2.The powder was introduced into the vessel with a blast of a gas mixture comprising nitrogen and methane produced by opening a solenoid valve connecting the vessel with a 2-gallon gas reservoir filled with nitrogen/methane gas mixture at 4,200 torr. Before each experiment, the gas mixture was prepared by evacuating the gas reservoir and re-filling it with 163 torr of methane and the balance of nitrogen. The duration of the gas blast pulse was 200 ms. At the end of the blast, the pressure in the vessel was close to 1 atm. To reduce the turbulence in produced gas powder mixture, the gas blast was followed by a

300 ms waiting period. Finally, the powder was ignited using an electrically heated tungsten wire placed in the center of the vessel. The combustion pressure traces were measured in real time using an American Sensor Technology AST 4700 transducer. The values and the rates of pressure rise produced by the combustion were compared for different powders.

A second set of experiments was carried out using a constant mass % of additive of each modifier in aluminum powder load and varying the methane concentration between 1.5 and 4.5 % while keeping the oxygen concentration constant.

Results and Discussion

A common concern for reactive metal powder addition is their sensitivity to electro-static discharge (ESD) ignition. All the materials used in this project were tested using a firing test system model 931 by Electro-tech Systems, Inc., according to standard Mil-1751A. Table 2 shows the measured values of the minimum ignition energy (MIE) for each material.

Table 1 Sensitivity of materials to electro-static discharge

Material	MIE (mJ)	Propagation
Spherical Al 10-14 micron	25.7	No
8Al+3CuO nanocomposite	3.8	Yes
8Al+MoO_3 nanocomposite	<0.8	Yes
2B+Ti nanocomposite	1.2	No
Al (10-14 micron) + 20%(8Al+3CuO) blend	13.2	No
Al (10-14 micron) + 20%(8Al+MoO_3) blend	6.9	No
Al (10-14 micron) + 20%(2B+Ti) blend	1.9	No

The data indicates that mixing the nanocomposites with the aluminum results in a powder that is more sensitive than pure aluminum but substantially less sensitive than nanocomposite material itself. In particular, it is worth noting that the flame did not propagate in the powder mixtures, unlike in the individual nanocomposite powders.

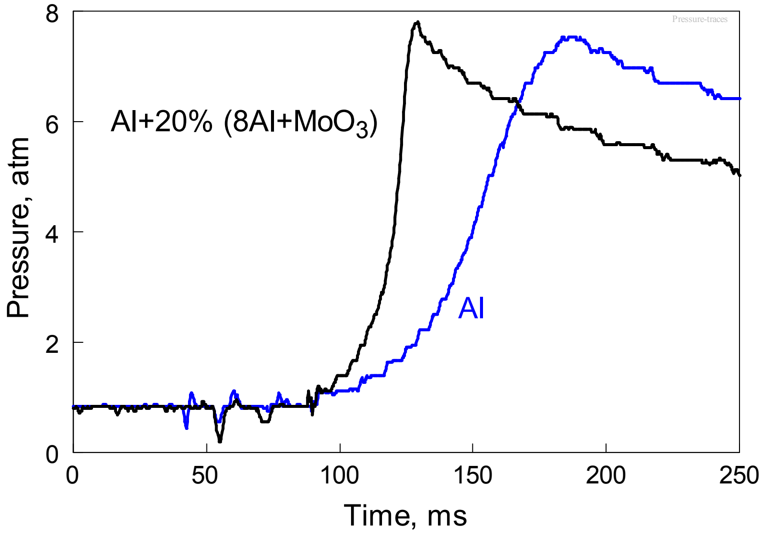

Figure 3 Constant volume explosion results obtained for regular aluminum powder and modified aluminum powder

Shown in Fig. 3 are two pressure traces from the CVE experiment. The modified aluminum powder shows both increased maximum pressure and rate of pressure rise. The accelerated burn rate was indeed observed for all experiments using nanocomposite powders as burn rate modifiers. However, the maximum pressure could be both higher and lower then for pure Al powder. The results are presented in Fig. 4 and 5.

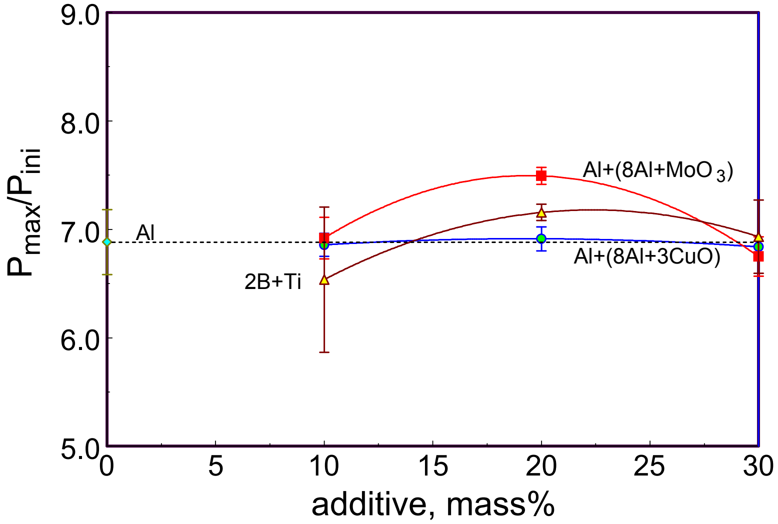

Figure 4 Normalized maximum pressure obtained using varying amounts of additives for 3% CH_4 21% O_2 and 76% N_2 atmosphere

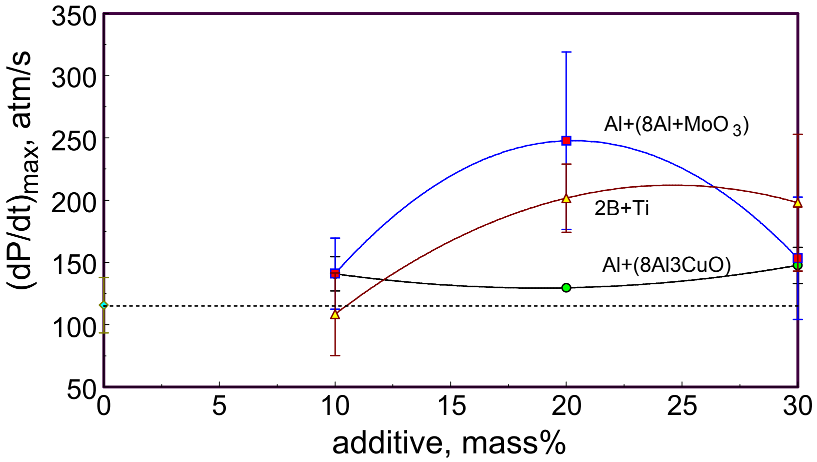

Figure 5 Maximum rate of pressure rise obtained using varying amounts of additives for 3% CH_4 21% O_2 and 76% N_2 atmosphere

Initial experiments were carried out to determine the effect of various amount of modifier. Figure 4 shows ratio of the maximum pressures observed in explosions over respective values of the initial gas pressure in the vessel. Results are shown for different modifiers at different additive mass percents. Pressure ratio shown in Fig. 4, P_{max}/P_{ini}, is proportional to the combustion temperature. Results for the maximum rates of pressure rise, $(dP/dt)_{max}$, are shown in Fig 5. The maximum rate of pressure rise, $(dP/dt)_{max}$, is proportional to the flame speed. The dashed lines in Figs. 4 and 5 indicate the reference values for pure aluminum powder. The data show that the most significant improvement was gained using 20 mass% additives for both $8Al+MoO_3$ and 2B+Ti nanocomposites. The effect is consistently small for 8Al+3CuO.

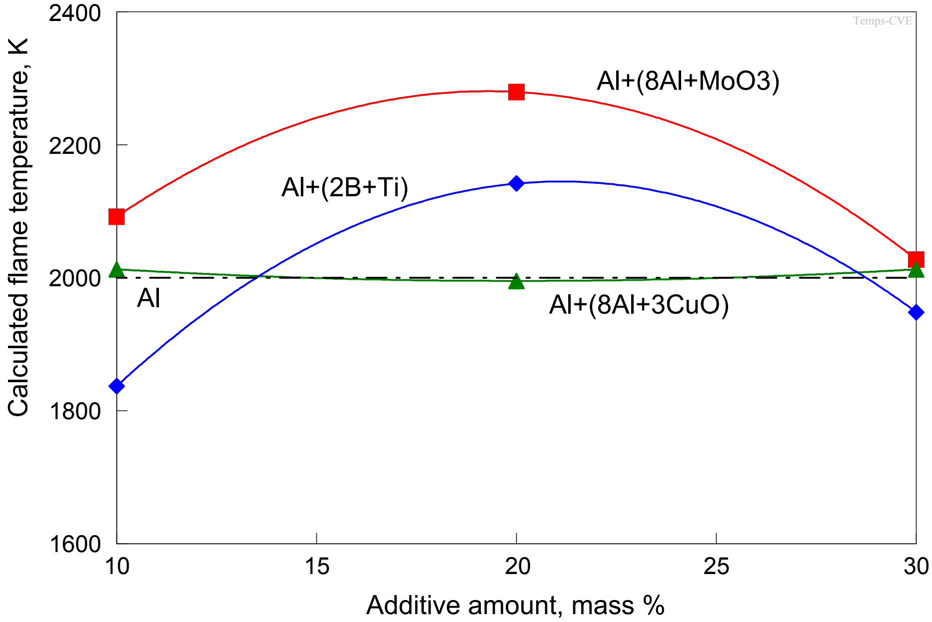

Figure 6 Combustion temperatures for different additives calculated using ideal gas law and maximum pressure recorded from CVE experiment

The combustion temperatures for different experiments were estimated from the measured pressures using the ideal gas law and neglecting the changes in the number of moles of gas in the vessel. The results for these estimates are presented in Figure 6. In agreement with the measured maximum pressures, the temperature increase over the case of pure Al is most significant when 20 % of $8Al+MoO_3$ was added to the aluminum powder.

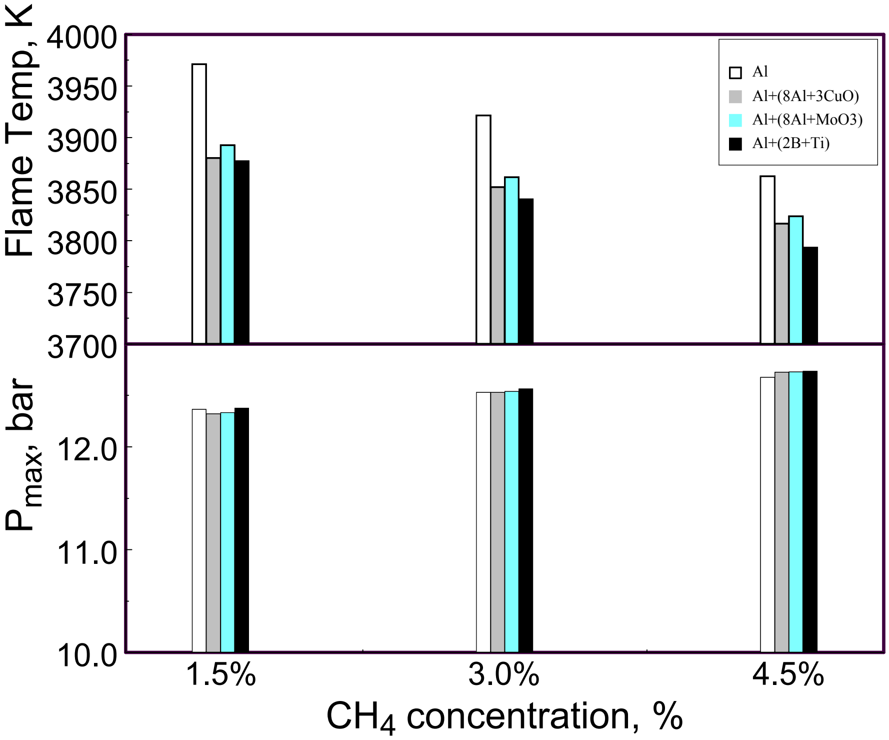

Figure 7 CEA calculations for pressure and flame temperature

Fig. 7 shows the calculated values for pressure and flame temperature using the NASA equilibrium code Chemical Equilibrium and Applications (CEA). The calculations were performed for constant volume combustion. Pure aluminum flames are characterized by substantially higher temperatures. However, the difference in the predicted pressure is much more subtle. The results indicate that there is a small increase in pressure with increasing methane concentration. The flame temperatures decrease with increasing methane concentration indicating a substantial change in the predicted make-up of the equilibrium combustion products. The calculations predict that the highest pressures are obtained by the 2B+Ti modifier followed by pure aluminum then the MoO_3 and finally the CuO.

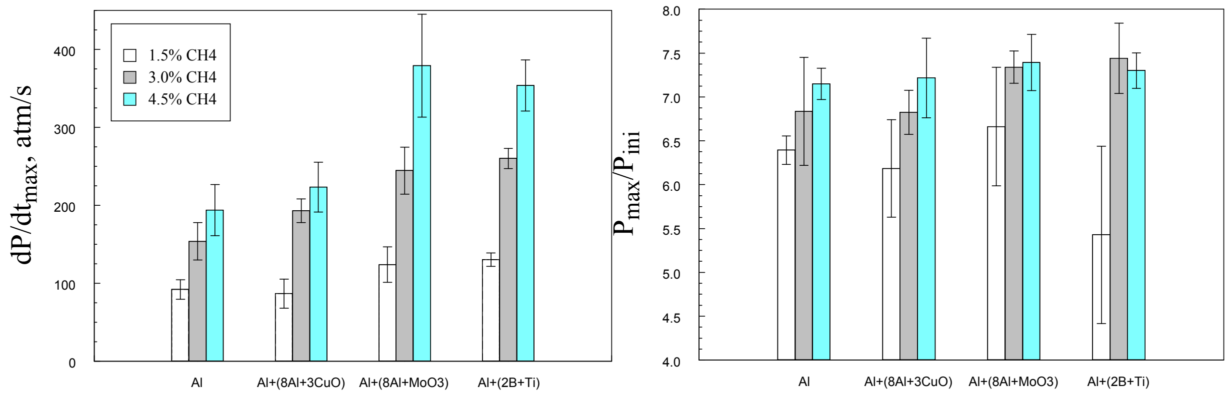

Figure 8 Constant volume explosion results for different atmospheres

Figure 8 shows the results of the CVE test in different environments of methane. There is an increasing trend in the combustion rate for all modifiers as the methane concentration increases. The most effective modifier seems to be the 8Al+MoO$_3$ or 2B+Ti depending on environment. The 8Al+3CuO on the other hand has little effect on the combustion performance. Similar to the CEA calculations, the 2B+Ti and MoO3 modifiers achieve the highest pressures. The CuO modifier has the lowest pressure of the modifiers.

The combustion products were collected and analyzed by energy-dispersive x-ray spectroscopy to determine the amount of aluminum and oxygen. This ratio was normalized by dividing it by the oxygen to aluminum ratio for an ideal reaction. Therefore, a ratio of 1 would indicate an ideal and complete reaction. The final normalized oxygen to aluminum ratio is shown in Fig. 9. Interestingly, it seems that the most complete reaction was achieved by the CuO modifier although it did not attain the highest pressure. The trend is followed for all three concentrations of methane.

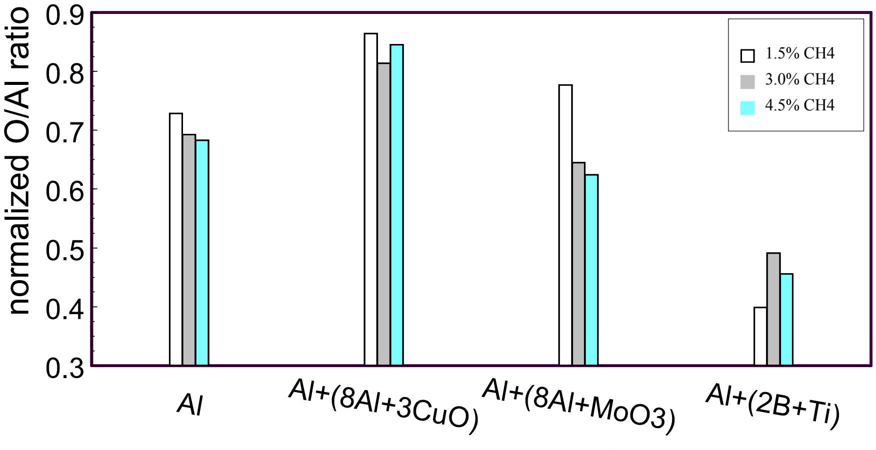

Figure 7 Oxygen to aluminum content ratio from analysis of combustion products

Conclusions

Addition of relatively small amounts of nanocomposite burn rate modifiers to a metal-oxidizer formulation enables substantial increase in the burn rate without a substantial reduction in the overall theoretical combustion enthalpy. In the present experiments, additives of nanocomposite aluminum-rich $8Al+MoO_3$ thermite and B-Ti materials were found effective in improving both the rate and maximum pressure of aluminum combustion. However, additives of a metal-rich nanocomposite $8Al+3CuO$ thermite did not show appreciable improvements in aluminum combustion.

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