A Thermal Study of Mixtures of Micron-sized Copper (II) Oxide, Aluminum and Magnalium

Richard Harrison

Avenue Research, Avenue House, The Avenue, Flitwick, MK45 1BP, UK

Abstract: *The reaction temperature in ignited samples of thermite compositions containing CuO and varying proportions of aluminum and magnalium was monitored at 1ms intervals by means of small embedded thermocouples. Analysis of the temperature profiles reveals that, in all cases, an exothermic minimum in the region of 950 K provides a significant contribution to the period from ignition to thermal runaway. The profiles were found to contain features that are attributable to both aluminum and magnesium (or magnalium) across the whole temperature range, indicating, in contrast to a commonly held belief about such mixtures, that the two metals were active participants at all stages of the reaction.*

Keywords: *Al-CuO thermite, Magnalium, Micron particles, Ignition*

Introduction

Thermites have proved to be highly versatile energetic materials, with applications in both military and civilian technologies; as such they have been a popular subject of research. In recent years the majority of that research has concentrated on nanothermites; that is, thermite compositions whose components have particle sizes in the nanometer to sub-micrometer range, because of their great versatility and high reactivity.[1–3] In comparison, there have been relatively few studies of thermites composed of micron-sized particles.

Aluminum has emerged as the principal fuel in nanothermites, largely because of the large enthalpy of formation of its oxide, its ready availability in suitable grades and the fact that its surface oxide coating provides a reasonable degree of stability at temperatures below the mixture's point of ignition. Energetically, magnesium is a viable alternative, but its lack of a protective surface layer of oxide means that its presence as nano-sized particles in a thermite is likely to render the mixture too unstable to be of practical value in the majority of cases.[4] Similar objections are likely to apply to magnalium (an alloy of magnesium and aluminum, usually in equal proportions by weight). Perhaps for this reason there has been little research into the behavior of CuO-based thermites containing magnesium and/or magnalium, despite the fact that such mixtures, if composed of micron-sized particles, are reliably stable – as is evidenced by their presence in many pyrotechnic compositions that are commonly found in fireworks.

In one of the few such studies, Hosseini et al.[5] investigated the reaction between micron-sized magnesium and nano-CuO. They reported an observed ignition temperature in the region of 900 K, comparable with that of Al-CuO nanothermite. In a later study[6] the same group of researchers investigated the effect of adding magnesium to an Al-CuO thermite, finding that it did not improve the initiation of the reaction, nor did it make any appreciable difference to the measured ignition temperature. The only significant effect they noted was an increase in the heat of reaction of the mixture, which may well have been the result of the additional metal content, but they made no comment on any possible reaction mechanism.

Existing studies of thermites that contain magnalium appear to have been restricted to sound-producing mixtures, such as pyrotechnic crackle compositions. In one of the earliest such studies, Shimizu[7] put forward the hypothesis that the magnesium component of the alloy is preferentially consumed in the early stages of the reaction. In addition, Koga et al.[8-10] examined the thermal behavior of mixtures of magnalium alloys with a range of metal oxides, and

also investigated the reactivity of the alloy alone when heated in air, up to a temperature of 1400 K. They claimed that their evidence indicated that the early stages of the reaction involved only magnesium, and that aluminum was not consumed until the temperature had risen to over 800 K. However, as discussed in a later section, an alternative interpretation of their results is possible. Other studies and descriptions of the behavior of pyrotechnic crackle compositions[11,12] appear – either implicitly or explicitly – to take Shimizu's hypothesis as a given fact.

A previous study[13] showed that the use of thermocouples to measure the temperature profiles of freely reacting samples of micron-sized Al-CuO thermite allowed qualitative conclusions to be made about the way the reaction progressed. The analysis produced data sets that are somewhat analogous to those resulting from other, more conventional thermal analysis techniques, including differential scanning calorimetry (DSC) and themogravimetric analysis (TGA). However, the analogy is far from exact, given that the self-heating rates are intrinsically highly variable and are also much more rapid – by a factor of the order of 1000 – than the constant, externally supplied rates used in DSC and TGA.

The purpose of the current study is to further investigate the value of using the same simple and direct temperature measurement technique to provide information about the nature of the progress of thermite reactions, in conditions that closely replicate those that occur in a pyrotechnic device. The specific objective is to investigate the changes that result from a progressive replacement of aluminum by magnalium. In addition, one further aim is to obtain evidence regarding the applicability of Shimizu's hypothesis to these mixtures.

Experimental Section

The copper oxide used in this study was obtained from Inoxia Ltd., Cranleigh, UK. It is of 98.5% purity and specified as passing an approximately 300 mesh screen, with a claimed particle size of less than 54 µm. Under x1000 magnification it was seen to consist of approximately spherical particles with sizes ranging from about 25 to 45 µm, together with a significant quantity of much smaller particles with sizes down to 1 µm or less. The aluminum, magnalium and resin binder were all supplied by PyroGarage, Crakow, Poland. The atomized aluminum was of 99.7% purity and nominally passed

325 mesh. It was seen to contain a mixture of particles with sizes ranging from 5 to 50 µm. The largest and smallest particles appeared irregular in shape but those of intermediate size were mostly spindle-shaped. The magnalium, a 50:50 alloy of unspecified purity, nominally passed 250 mesh and was found to consist of a mix of angularly shaped particles, most of which had dimensions in the range from 20 to 70 µm. The alcohol-activated binder is a phenol formaldehyde (phenolic) resin, also of unspecified quality, that nominally passes 325 mesh.

The Type G thermocouples consist of a five-turn twisted pair of 0.1 mm diameter tungsten and tungsten-rhenium alloy (26 wt% Re) wires that were obtained from Goodfellow Cambridge Ltd. The twisted junction was spot welded to ensure good, permanent contact, and bent double at its midpoint to minimize its length, thereby ensuring that the junction is well embedded within the reacting grain. At the 'cold' junction, the wires were crimped to copper leads that were mounted on an insulating support. An example assembly is illustrated in Figure 1 (A) and (B).
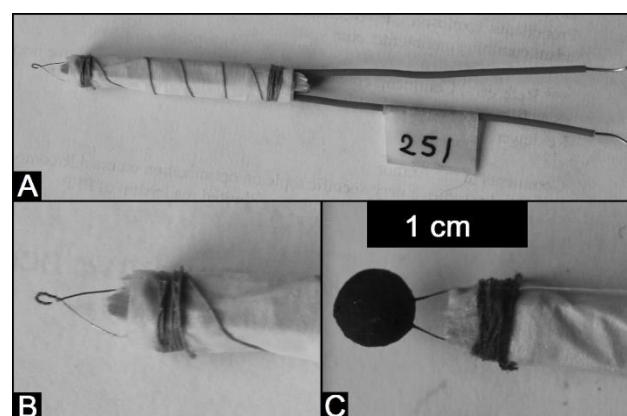

Figure 1. Thermocouple construction:
(A) Completed assembly, before dipping. The label provides a unique ID for each sample and also indicates the thermocouple's polarity.
(B) Detailed view of the twisted pair junction.
(C) A completed and primed grain.

Each sample grain was formed by repeatedly dipping a weighed thermocouple's junction in an alcoholic slurry of the appropriate composition until it was approximately 3mm in diameter, completely enclosing the junction. Once dry, the grain was dipped in a water-based slurry of a priming composition until the prime coating was about one millimeter thick. The assembly was weighed and photographed at the completion of each stage so that the mass and diameter of both the grain and its coating of prime were known. A typical grain, as

shown in Figure 1 (C), had a mass of 60 to 70 mg, with a density close to 50% of the theoretical maximum, and was coated in about 80 mg of prime.

In order to obtain good resolution across the entire temperature range, a completed thermocouple assembly was connected to a DC amplifier with three channels of output, at gains of 100, 200 and 400 respectively. An Arduino Uno was used to perform the A/D conversions and transmit the data via a Bluetooth link to a Raspberry Pi, which ran the controlling software. It also used published tabular data[14] to perform the voltage to temperature conversion and wrote the results to file, for later analysis.

All the trials were conducted in air. Each primed grain was ignited by a brief burst of flame from a blowtorch, after which no further external heat was supplied. The grain's internal temperature was measured at one millisecond intervals as the reaction proceeded from ignition to conclusion. Despite the relative simplicity of the apparatus, the measured temperatures were found to be accurate to within 10 K or better, at all rates of change of temperature – which typically vary from a low value in the region of 100 K/s, to in excess of 10^6 K/s at thermal runaway. Audio and video records were made of each trial, using a Panasonic HC-X900 camera, operating at 25 fps and with a fixed audio gain.

The data analysis was performed by custom software that uses a 5-point binomial filter to provide some reduction of the noise level in the temperature readings and then calculates the rate of energy release, P, at each measured point:

$$P \simeq m \cdot c \cdot \Delta T / \Delta t$$

where Δt is the time interval between successive measurements, ΔT is the change in temperature over that interval, m is the mass of the grain and c is the weighted mean of the heat capacities of the grain's constituents. The calculation takes into account estimates of the heat lost to the surroundings, based on the cooling curves of grains that reacted but did not explode. It also compensates for estimated changes in the heat capacity resulting from the change in composition as the reaction progresses. Both of these corrections turn out to be relatively small and could be omitted. Perhaps more significantly, the calculation ignores how any of the physical properties of the materials vary with temperature, which has the effect of slightly underestimating the release of energy at higher temperatures. However, bearing in mind the intrinsic

noisiness of the raw data and the fact that the subsequent analysis of the data depends on relative rather than absolute values, this factor is not believed to have a significant effect on the overall nature of the results or their interpretation. To eliminate the effect of the variation of the grains' masses from sample to sample, the thermal output data are presented in terms of a quantity Q:

$$Q = P/m$$

in units of J/g/ms or, more concisely, kW/g.

Results and Discussion

The Reference Composition

The behavior of this composition – consisting of -300 mesh copper (II) oxide (81%) and -325 mesh atomized aluminum (19%) and an additional 3% of phenolic resin – was described previously.[13] As in that earlier study, a combination of the video recordings and the temperature measurements indicates that the burning prime provided significant amounts of heat for up to two seconds, by which time the grain's temperature was raised to between 500 and 600 K. From that point onwards, reactions within the thermite grain itself became the dominant energy source. This was found to be the case for all the compositions investigated in the current study.
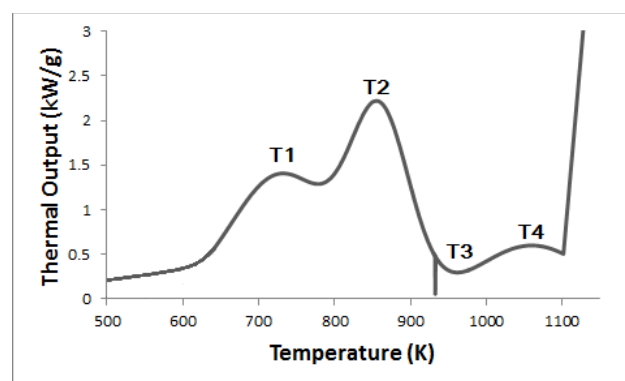
Figure 2. Schematic energy-temperature profile for the reference composition. Labels T1 to T4 mark features that are discussed in the text. The sharp spike in the region of 930 K is caused by the melting of aluminum.

As illustrated schematically in Figure 2, when the rate of energy release is plotted against temperature, the most significant features are the existence of two partially resolved exothermic peaks (T1, T2) that consistently appeared at temperatures of about 720 K and 840 K, a local minimum (T3) at a slightly higher temperature than the melting point of aluminum and a third peak (T4) at around 1060 K. The data provided indirect evidence for the existence of a fourth peak

in the region of 1260 K. However, since that temperature is comparable with that at which the transition to an explosive thermal runaway begins, this peak was never directly observed.

The temperatures at which the peaks occur were shown to correlate well with those found by Umbrajkar et al.[15] in their thermal study of a closely stoichiometric Al-CuO nanocomposite, provided that the very different rates of change of temperature in the two studies were taken into account. However, it must be pointed out that the relative intensities they observed do not match those found in either the current or the earlier study, nor did their findings show such a pronounced minimum, at T3, between the second and third exothermic peaks. In general, the peaks observed in the analysis of the self-heated samples appear to be better resolved than those seen in the DSC measurements.

Some progress has been made in modeling the reactions, both in terms of the processes leading to ignition[16–18] in Al-CuO nanocomposites, and at higher temperatures in fully ignited micron-sized mixtures.[19] However, as pointed out by Comet et al.[4] and Catoire,[20] there is still much that is only partially understood. In addition, it is not clear to what extent the nanocomposite findings will apply to mixtures containing micron-sized particles. A determination of the kinetic parameters for each of the observed reaction steps would be a great aid to resolving this issue. However, the intrinsic variability and uncontrolled nature of the internally generated heating rates mean that standard techniques, such as isoconversion methods – which depend on controllable, constant externally applied rates of heating – are not applicable.

Despite these uncertainties, it seems reasonable to consider that the features shown in Figure 2 provide characteristic indicators of the reaction between micron-sized particles of aluminum and copper (II) oxide. In this study, features T1, T2 and T4 are used as such a 'fingerprint'.

The Role of Magnalium

Table 1 lists the seven approximately stoichiometric compositions that were tested, with composition A being the reference composition that was discussed in Section 3.1. Composition G contains magnalium as the only fuel and compositions B to F are mixtures with gradually increasing proportions of magnalium.

Table 1. *Seven compositions with differing relative proportions of aluminum and magnalium.*

Material	A	B	C	D	E	F	G
CuO	81	81	81	81	80	80	80
Al	19	16	14	13	10	7	0
Magnalium	0	3	5	6	10	13	20
Phenolic Resin	+3	+3	+3	+3	+3	+3	+3

Table 2 gives the makeup of the prime that was used with all seven compositions, based on an informally published crackle prime of Spanish origin. It is designed to burn relatively slowly, with the generation of a hot slag that both efficiently transfers heat to the core and subsequently reduces heat losses to the surroundings.

Table 2. *Priming composition.*

Material	%
KNO_3	45
Magnalium, -350 mesh	15
PVC	12
Charcoal, airfloat	9
Fe_3O_4	9
Sulfur	6
Dextrin	4

Figure 3 shows a comparison of the variation of temperature with time for the reference composition (A) and for composition G. The overall similarity in form of the two curves – a broad similarity that was shared by all the compositions that were studied – suggests that similar mechanisms may be in operation, irrespective of the presence or absence of magnalium.
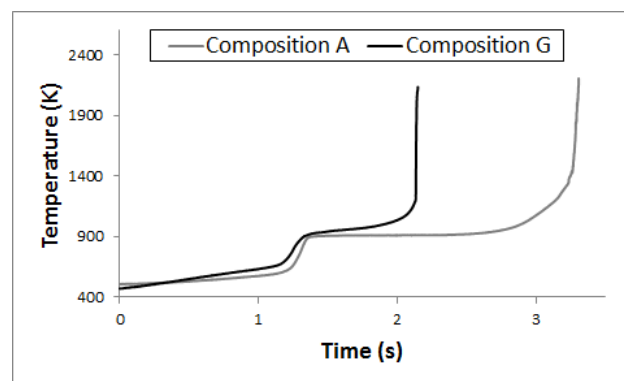

Figure 3. *A comparison of the variation of temperature with time for compositions A and G.*

An obvious difference is the length of time that the different compositions spend at a temperature of around 900 K. For the reference composition, the strong nature of this feature was attributed to the energy consumed by the melting of aluminum, combined with a particularly low rate of energy release around that temperature. Bearing in mind

the absence of aluminum in composition G, the observed reduction in the dwell time is to be expected, provided that the presence of magnalium does not significantly change the rate of energy release in this temperature range. In fact, there was a general tendency for those compositions containing a smaller proportion of aluminum to spend less time at this temperature. However, the correlation was relatively weak, suggesting that that there may be other significant factors affecting this feature.

None of the compositions showed any evidence of a similar plateau in the region of 733 K, the melting point of magnalium. This may be the result of two factors that will tend to mask any such feature; that, as an alloy, magnalium has a less well defined melting point than a pure substance so the phase transition will take place over a finite temperature range, and that the rate of energy release at that temperature is greater – by as much as a factor of ten in some cases – than in the region of 933 K.

Despite the overall similarity in behavior, the graphs of thermal output against temperature for compositions B to G reveal some significant differences at temperatures below 950 K when compared with the reference composition. For compositions B to F, where both aluminum and magnalium were present, the profile in this temperature range was most accurately reproduced when, in addition to T1 and T2, a third component, labeled T5 in Figure 4 and centered close to 800 K, was included. As was found for the reference composition's two components, the relative amplitudes of these features varied somewhat unpredictably from sample to sample. In addition, there was no clear correlation between the relative amplitudes and the proportion of magnalium in the mixtures. But, once again, there was a remarkable consistency in the temperatures at which peaks T1, T2 and T5 occurred.

In the case of composition G, the variation of the thermal output at temperatures below 950 K had the appearance of a single broad exotherm centered at a temperature close to 800 K. Although there may be weak indications of very poorly defined components that approximately correspond to T1 and T2, they could not be resolved with any degree of certainty.
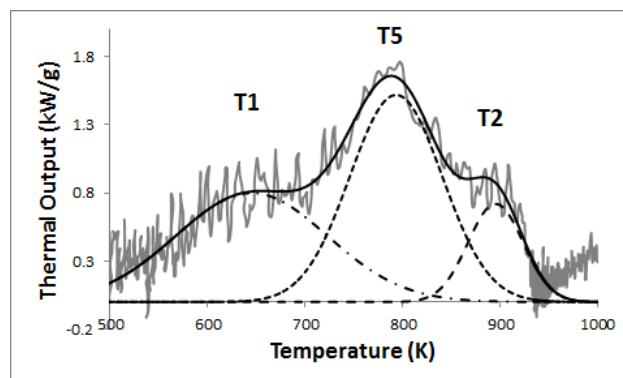

Figure 4. *Empirical fit of the sum (solid line) of three Gaussian distributions (dotted lines) with an observed energy-temperature profile for composition B.*

The location of the notable minimum, T3, was also measured for all seven compositions. As with other features, the thermal output at this minimum was found to be somewhat variable, generally lying in the range from 0.1 to 0.3 kW/g. It seems likely that this variability from sample to sample might be the reason for the previously noted lack of a clear correlation between the aluminum content and the time spent close to its melting point. However, the temperature at which this minimum occurred was found to be remarkably consistent from sample to sample, and across all the compositions.

The exothermic peak (T4) in the region of 1050 to 1100 K, which was reasonably well defined for the reference composition, tended to be obscured in compositions B to F by the rise in temperature leading to the transition to the explosive phase. In its early stages, that rise was significantly less abrupt than in the reference composition, which may be an indication that the presence of magnalium causes an additional exothermic feature with a peak temperature of 1200 K or more. Nevertheless, there was a reasonably good level of consistency in the temperature at which feature T4 occurred across all the samples for which its position was measurable. Table 3 lists the temperatures at which all five measurable features were seen to occur in each composition.

Table 3. *Measured temperatures for features T1 to T5 for compositions A to G. A dash indicates that the feature was undetectable; a question mark indicates that the feature appeared to be present, but was not sufficiently clearly defined for its position to be determined.*

Comp	T1 (K)	T2 (K)	T3 (K)	T4 (K)	T5 (K)
A	718±20	840±20	948±10	1057±25	-
B	679±25	882±20	953±15	1121±20	793±20
C	720±20	873±10	946±10	1097±40	803±20
D	702±20	864±20	948±10	1074±20	781±20
E	714±20	852±20	966±25	1117±25	809±20
F	695±30	864±20	955±25	?	789±20
G	?	?	955±15	-	803±15

With the exception of compositions F and G, the features T1, T2 and T4 were present for all samples. In the case of composition F, the start of the explosive transition was consistently at such a low temperature that peak T4 was always partially obscured and its position was therefore unmeasurable. The transition temperature was even lower for composition G and there was little or no evidence of the existence of feature T4.

There was a noticeable tendency for the transition to the explosive phase – taken to be the temperature at which the temperature-time curve made its final, abrupt increase in steepness – to occur at progressively lower temperatures as the proportion of magnalium increased. As had also been noted in the earlier study of the reference composition[13] there was, in all cases, some variation from sample to sample in the temperature at which the transition occurred, but the average value for each composition, when plotted against the magnalium content, revealed the consistent trend shown in Figure 5.
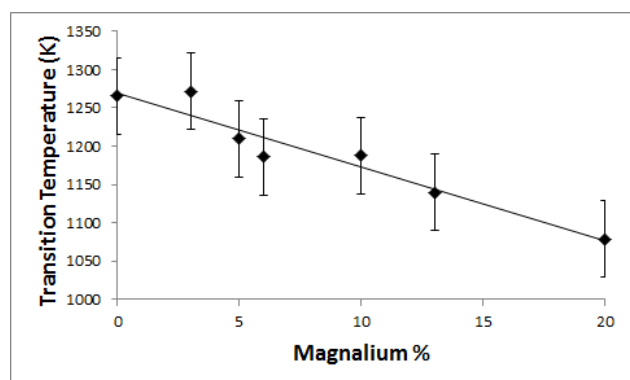

Figure 5. *The variation in the temperature of the transition to the explosive phase, with respect to the composition's magnalium content. The error bars represent an estimate of the standard deviation for each measurement.*

The transition temperature for composition A, at 1270 ± 20 K, is close to what others have measured as the ignition temperature[21] or the reaction onset temperature[22] for Al-CuO thermites of broadly similar morphology. The transition temperature falls to 1080 ± 20 K for composition G, whose only metallic fuel is magnalium.

In all cases, audio data extracted from the video recordings showed that the explosive transition was associated with a rapid rise in amplitude over a period lasting only a few tenths of a millisecond. This pattern of behavior, which had previously been observed for the reference composition,[13] indicates that the onset of gas production was abrupt – as has been found by others for Al-CuO mixtures.[23] This rise was followed by a relatively slow decay over a period of several tenths of a second, implying that the explosive reaction takes place over an extended period of time, rather than involving the whole grain in the same instant. Since magnesium is absent in composition A and must be present at this stage in (at least) compositions E and F, it seems reasonable to conclude that the presence or absence of magnalium does not change the overall progress of the explosive phase.

The Shimizu Hypothesis

In his study of pyrotechnic strobes, Shimizu[24] put forward the hypothesis that the smolder and flash phases were the result of separate low and high temperature reactions, involving either two different oxidizers or two different fuels or both. This was a generalization of the findings of Wasmann[25] and Krone[26] who, although studying two very different types of strobe composition, both proposed a two-part chemical mechanism. In particular, Krone reported that the analysis of a partially reacted magnalium-based pyrotechnic strobe composition revealed it to contain aluminum, but only traces of magnesium, and concluded that magnesium must have been preferentially consumed in the initial smolder stage. Shimizu may also have been influenced by a study by Popov et al.[28] of the behavior of Mg-Al alloy particles when ignited in air or an oxidizing flame. The authors reported that the particles burned in a two-stage process, with magnesium being consumed in the first stage.

In a later study of the reaction of pyrotechnic crackle compositions composed of magnalium, aluminum and metal oxides, Shimizu[7] relied on this kind of evidence to put forward a more specific form of his hypothesis; that the early, smolder stage in these

compositions was the result of a preferential oxidation of the magnesium content of the magnalium and that the fuel for the explosive phase was principally aluminum, together with any remaining magnesium. It is this form of the hypothesis that is the topic of discussion in this section.

The main evidence that Shimizu relied on to support his view is that provided by Krone's analysis.[26] However, as pointed out by Dreizin and Schoenitz,[27] samples can continue to react during cooling, so such analyses are unlikely to represent the actual state of the reaction at elevated temperatures. In the case studied by Krone, it is certainly possible that both metals may have been involved in the initial reaction, but that Al_2O_3 could have been slowly reduced by any remaining magnesium during the period before the sample had cooled to room temperature. The same objection cannot be applied to the findings of Popov et al.[28] However, more recent studies by Aly et al.,[29,30] of in-air laser ignition of alloy particles, showed that two-stage burning was evident only in the case of particles that were formed by a mechanical alloying process, and not seen to occur with particles made from a melted and cast alloy. The authors concluded that, in the mechanically alloyed case, the early consumption of magnesium was the result of its evaporation from the surface of unalloyed inclusions. Not only do such inclusions not exist in cast alloys, but there is also evidence[31] that the vapor pressure of Mg above such alloys is less than would be expected, given their magnesium content.
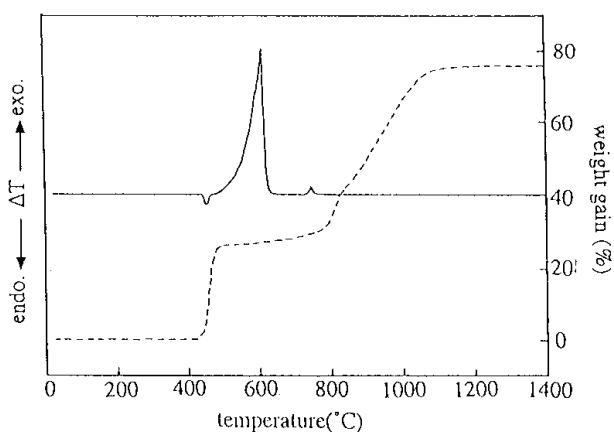

Figure 6. *DSC (full line) and TGA (dotted line) data for a sample of magnalium, heated in air at 10 °C/min. Reproduced from Koga et al.[10]*

Later evidence was provided by Koga et al.[8-10] who, as was mentioned in the Introduction, investigated the thermal behavior of mixtures of magnalium with a number of metal oxides. In one of their papers[10] they presented the DSC and TGA scans of a heated sample of a magnalium that are reproduced in Figure 6. The TGA curve indicates that there appear to be two major phases of oxidation. The first starts close to the melting point of the alloy, at about 450°C (723 K) resulting in about a 30% gain in weight, and the second occurs between about 800 and 1100°C (1073 and 1373 K) with a total increase in weight of about 75%.

The authors claimed that the first increase is compatible with the oxidation of just the magnesium content, but their quoted calculated weight increase of 32.9% is correct for a 50:50 alloy and not for the 30:70 Mg:Al alloy that they claim to have used. The observed overall weight gain is also compatible with the calculated value (77.4%) for a 50:50 alloy. If it is assumed that the authors misidentified the alloy's composition and the data in Figure 6 was actually obtained for a 50:50 alloy, then these results appear to provide strong support for the idea that magnesium is preferentially oxidized in the initial stage of the reaction.

However, it must be pointed out that these results are subject to the same criticism that was applied to Krone's chemical analysis. At the stated heating rate of 10°C/min, it takes about half an hour to raise the temperature from room temperature to 600°C. If, during that stage, any Al_2O_3 were to form, there would easily be time for it to be reduced by any remaining elemental magnesium. Such considerations indicate that it is almost inevitable that the TGA curve should be of the observed form. In that case, it is unlikely to provide useful information about reactions that occur on the enormously shorter timescales that are typical for freely burning pyrotechnic compositions.

The above discussion suggests that the evidence in support of Shimizu's hypothesis as regards mixtures of magnalium and metal oxides is much weaker than it appears to be at first sight. In addition, there are other research results that suggest it may be false. Given that both aluminum and magnesium are, individually, highly reactive, the truth of the hypothesis should imply that aluminum oxide is reduced rapidly and efficiently by magnesium. But Shimizu himself noted that the reaction between Mg and Al_2O_3 'propagated very slowly … without a flame'. McLain[32] provides evidence that the direction of the reaction reverses at a temperature of about 1920 K so that, above that temperature, aluminum will be likely to reduce magnesium oxide. Furthermore, Grjotheim et al.[33] report that, in the

temperature range 1120 to 1400 K, aluminum can reduce magnesium oxide by means of the reaction:

$$2Al + 4MgO \rightarrow MgAl_2O_4 + 3Mg$$
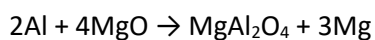
Taken together, these observations suggest that preferential consumption of either metal is not likely to occur to any significant degree in the relatively short time that a thermite reaction takes to run to completion. In the current study, the presence of features T1, T2 and T4 appears to be good evidence that aluminum was taking part in the reaction throughout the temperature range, from 700 K or lower to 1100 K and above, regardless of the presence or absence of magnalium. That T5 was present only for compositions containing magnalium, and the dependence of the starting temperature of the explosive phase on the magnalium content, appear to be strong indicators that magnalium was also involved in the reaction at temperatures around 800 K, and also between 1100 and 1200 K.

There was no significantly measurable dependence of the strength of the T5 exotherm on the magnalium content over the entire range, from 3 to 20 percent. That this feature figured prominently in a composition containing as little as 3 percent of magnalium may indicate that magnalium is a more effective fuel at low temperatures. This might not be unreasonable, given its much lower melting point relative to aluminum. But, in contrast to what would be expected if Shimizu's hypothesis were valid in this case, the data provides no evidence that either magnesium or aluminum was being preferentially consumed to any significant degree at any stage of the process.

Conclusions

This paper describes the use of a simple, direct temperature measurement technique, under conditions similar to those found in pyrotechnic devices, to investigate the effect of including increasing proportions of magnalium in a previously studied closely stoichiometric Al-CuO composition. When magnalium was present, the progress of the reaction was found to be significantly different from that deduced by Koga et al.[10] from their TGA measurements, which were made at the low, constant heating rates that are characteristic of conventional thermal analysis techniques.

A notable feature, shared by all seven compositions, regardless of the relative proportions of aluminum and magnalium, is a pronounced minimum of exothermic activity (T3) in the region of 950 K, close to, but not coincident with the melting point of aluminum. This minimum is a major contributor – together with the time required to melt any elemental aluminum that is present in the mixture – to the delay between ignition and explosion. Such a pronounced minimum has not been observed in thermal studies of Al-CuO nanocomposites; it may indicate a significant difference in the reaction mechanism that could be the consequence of either the faster and more variable rate of change of temperature or the much greater particle size in the compositions used for this study.

Despite these uncertainties, the stable presence of features T1, T2 and T4 in all the compositions that were studied – with the possible exception of composition G, which contains only magnalium – appears to be evidence that elemental aluminum takes part in the reactions that occur throughout the temperature range. For compositions that contained both aluminum and magnalium, the additional presence of feature T5 and the dependence of the explosive transition temperature on the magnalium content imply that magnalium, or the magnesium that it contains, also participates in the reactions at all temperatures. There is no evidence of a significant degree of preferential consumption of either metal at any stage, which indicates that, in this case, Shimizu's hypothesis does not apply.

The rapid and highly variable internally generated heating rate means that standard isoconversion techniques cannot be used to evaluate the relevant reaction parameters. In consequence, the reported results are of a somewhat qualitative nature. Further work is required to determine whether other techniques can be used to obtain reliable estimates of the reactions' kinetic parameters.

References

1   M. L. Pantoya, J. J. Granier, Combustion Behavior of Highly Energetic Thermites: Nano versus Micron Composites, *Propellants, Explosives, Pyrotechnics*, Vol. 30, 2005, pp. 53-62.

2   R. A. Yetter, G. A. Risha, S. F. Son, Metal particle combustion and nanotechnology, *Proc. Combust. Inst.*, Vol. 32, 2009, pp. 1819-1838.

3   I. Monk, M. Schoenitz, R. J. Jacob, E. L. Dreizin, M. E. Zachariah, Combustion Characteristics of Stoichiometric Al-CuO Nanocomposite Thermites Prepared by Different Methods,

Combustion Science and Technology, Vol. 189, 2017, pp. 555–574.

4 M. Comet, C. Martin, F. Schnell, D. Spitzer, Nanothermites: A short Review. Factsheet for Experimenters, Present and Future Challenges, *Propellants, Explosives, Pyrotechnics*, Vol. 44, 2019, pp. 18-36.

5 S. G. Hosseini, A. Sheikhpour, M. H. Keshavarz, S. Tavangar, The effect of metal oxide particle size on the thermal behavior and ignition kinetic of Mg–CuO thermite, *Thermochimica Acta*, Vol. 626, 2016, pp. 1–8.

6 A. Sheikhpour, S. G. Hosseini, S. Tavangar, M. H. Keshavarz, The influence of magnesium powder on the thermal behavior of Al–CuO thermite mixture, *Journal of Thermal Analysis and Calorimetry*, Vol. 129, 2017, pp. 1847–1854.

7 T. Shimizu, Studies on Mixtures of Lead Oxides with Metals (Magnalium, Aluminum or Magnesium), *Pyrotechnica*, Vol. XIII, 1990, pp. 10-18.

8 M. Koga, M. Matsumoto, S. Yoshinaga, A. Miyahara, Thermal behavior for mixture of red lead, copper oxide and magnalium. Part 2. Study on sounding body, *Journal of the Japan Explosives Society*, Vol. 57, 1996, pp. 192-197.

9 M. Koga, M. Matsumoto, S. Yoshinaga, A. Miyahara, Thermal behavior of the mixtures of copper oxide, nickel oxide and magnalium. Part 3. Study on sounding body, *Journal of the Japan Explosives Society*, Vol. 57, 1996, pp. 198-203.

10 M. Koga, A. Miyahara, M. Matsumoto, K. Miyano, S. Yoshinaga, Thermal behavior of the mixtures of metal oxide and magnalium, *Proceedings of the 23rd International Pyrotechnics Society Seminar*, 1997, pp 346-356.

11 A. P. Hardt, Pyrotechnics, Pyrotechnica Publications, Post Falls Idaho, 2001, p. 159.

12 C. Jennings-White, Strobe Chemistry, in *Pyrotechnic Chemistry*, Journal of Pyrotechnics Inc., Whitewater CO, 2004, ch. 15 p. 7.

13 R. Harrison, A Thermal Study of a Simple Al-CuO Pyrotechnic Crackle Composition, *Propellants, Explosives, Pyrotechnics*, Vol. 44, 2019, pp. 733-743.

14 F. R. Caldwell, Thermocouple Materials, NBS Monogr. (U. S.) 40, 1962, p. 34.

15 S. M. Umbrajkar, M. Shoenitz, E. L. Dreizin, Exothermic reactions in Al-CuO nanocomposites, *Thermochimica Acta*, Vol. 451, 2006, pp. 34-43.

16 A. Ermoline, M. Shoenitz, E. L. Dreizin, Reactions leading to ignition in fully dense nanocomposite Al-oxide systems, *Combustion and Flame*, Vol. 158, 2011, pp. 1076-1083.

17 A. Ermoline, D. Stamatis, E. L. Dreizin, Low-temperature exothermic reactions in fully dense Al-CuO nanocomposite powders, *Thermochimica Acta*, Vol. 527, 2012, pp. 52-58.

18 D. Stamatis, A. Ermoline, E. L. Dreizin, A multi-step reaction model for ignition of fully-dense Al-CuO nanocomposite powders, *Combustion Theory and Modelling*, Vol. 16, 2012, pp. 1011-1028.

19 S. Knapp, V. Weiser, S. Kelzenberg, N. Eisenreich, Modeling Ignition and Thermal Wave Progression in Binary Granular Pyrotechnic Compositions, *Propellants, Explosives, Pyrotechnics*, Vol. 39, 2014, pp. 423-433.

20 L. Catoire, Detailed Chemical Kinetic Models for Nanothermites, *Propellants, Explosives, Pyrotechnics*, Vol. 44, 2019, pp. 41-46.

21 K.Ilunga, O.del Fabbro, L.Yapi, W.W.Focke, The effect of Si-Bi2O3 on the ignition of the Al-CuO thermite, *Powder Technology*, Vol. 205, 2011, pp. 97-102.

22 V. S. Parimi, S. Huang, X. Zheng, Enhancing ignition and combustion of micron-sized aluminum by adding porous silicon, *Proceedings of the Combustion Institute*, Vol. 36, 2017, pp. 2317-2324.

23 G. C. Egan, K. T. Sullivan, T. Y. Olson, T. Yong-Jin Han, M. A. Worsley, Ignition and Combustion Characteristics of Nanoaluminum with Copper Oxide Nanoparticles of Differing Oxidation State, *Journal of Physical Chemistry C*, Vol. 120, 2016, pp. 29023-29029.

24 T. Shimizu, Studies on Strobe Light Pyrotechnic Compositions, *Pyrotechnica*, Vol. VIII, 1982, pp. 5-28.

25 F. Wasmann, Pulsierend Abbrennende Pyrotechnische Systeme, in: *Pyrotechnik: Grundlagen, Technologie und Anwendung*, Institut für Chemie der Treib- und Explosivstoffe (Fraunhofer Gesellschaft), Karlsruhe, 1975, pp. 239-250.

26 U. Krone, Strahlungsemission in Intervallen – Oscillierende verbrennung pyrotechnischer Satze, in: *Pyrotechnik: Grundlagen, Technologie und Anwendung*, Institut für Chemie der Treib- und Explosivstoffe (Fraunhofer Gesellschaft), Karlsruhe, 1975, pp. 225-237.

27 E. L. Dreizin, M. Schoenitz, Correlating ignition mechanisms of aluminum-based reactive materials with thermoanalytical measurements, *Progress in Energy and Combustion Science*, Vol. 50, 2015, pp. 81-105.

28 E. I. Popov, L. Y. Kashporov, V. M. Mal'tsev, A. L. Breiter, Combustion Mechanism of Aluminum-Magnesium Alloy Particles, *Combustion, Explosion and Shock Waves* (Engl. Transl.), Vol. 9, 1973, pp. 204-208.

29 Y. Aly, M. Schoenitz, E. L. Dreizin, Ignition and combustion of mechanically alloyed Al-Mg powders with customized particle sizes, *Combustion and Flame*, Vol. 160, 2013, pp. 835-842.

30 Y. Aly, E. L. Dreizin, Ignition and combustion of Al·Mg alloy powders prepared by different techniques, *Combustion and Flame*, Vol. 162, 2015, pp. 1440-1447.

31 Z. Moser, W. Zakulski, K. Rzyman, W. Gasior, Z. Panek, I. Katayama, T. Matsuda, Y. Fukuda, T. Iida, Z. Zajaczkowski, J. Botor, New Thermodynamic Data for Liquid Aluminum-Magnesium Alloys from emf, Vapor Pressures, and Calorimetric Studies, *Journal of Phase Equilibria*, Vol. 19, 1998, pp. 38-47.

32 J. H. McLain, *Pyrotechnics from the Viewpoint of Solid State Chemistry*, The Franklin Institute Press, Philadelphia, 1980, p. 87.

33 K. Grjotheim, O. Herstad, J. M. Toguri, The Aluminum Reduction of Magnesium Oxide, *Canadian Journal of Chemistry*, Vol. 39, 1961, pp. 443-450.