

A Thermal Study of a Simple Al–CuO Pyrotechnic Crackle Composition

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Abstract: The reaction temperature in ignited samples of a novel, chemically simple pyrotechnic crackle composition was monitored at 1 ms intervals by means of a small embedded thermocouple. Analysis of the results reveals that an exothermic reaction is detectable at temperatures as low as 500 K. The reaction is found to progress in at least three – and probably four – steps that correlate well with similar findings from the study of nanocomposites of the same

composition. The first two steps are shown to be associated with the crackle's delay phase. The transition to the explosive phase is shown to occur at a temperature significantly above the melting point of aluminum, being triggered at or beyond the temperature of operation of the third reaction step. The results provide a behavioral baseline for the future study of more complex crackle compositions.

Keywords: Pyrotechnic crackle · Al–CuO thermite · Micron particles · Ignition

1 Introduction

Pyrotechnic crackle is made from a thermite-like mixture of powdered metals and metal oxides, where all the particles are micron-sized. When formed into granules with the aid of an organic binder, the characteristic behavior is that, after ignition, there is a delay period during which a crackle granule starts to glow, followed by an explosion. When ejected in large numbers from a pyrotechnic device, they produce a cloud of flashes, accompanied by a series of reports that merge into a sharp crackling sound.

The effect appears to have originally been developed in China, at some time in the 1980s, based on a mixture of lead (II,IV) oxide and an alloy of aluminum and magnesium in equal parts by weight (magnalium). According to Michael S. Swisher [1] crackle's first known appearance in the West was at the 1988 Pyrotechnics Guild International (PGI) Convention, where one of the class C vendors was offering for sale a Chinese consumer firework device called "Dragon's Eggs".

Swisher's subsequent investigation led to replication of the effect with a closely stoichiometric mixture of lead (II,IV) oxide and magnalium, bound with a solution of nitrocellulose (NC). The initial choice of an NC binder was to ensure the continued structural integrity of the crackle grains when they were embedded in a black powder based matrix – which generally uses a water-activated binder such as dextrin – to form crackling comets.

Swisher communicated his findings to Takeo Shimizu, who undertook a detailed study of the topic, resulting in his seminal 1990 paper [2]. In that investigation, Shimizu found NC to be more effective than his other binder of choice, glutinous rice starch. Based on the results of his experiments, Shimizu put forward the hypothesis that the delay

(or, in his terms, the 'dark reaction') is "due to a surface oxidizing reaction of the aluminum particles, or due to an oxidizing reaction of magnesium in the magnalium alloy with the lead oxide". It seems likely that Shimizu's interpretation was strongly influenced by his earlier study [3] of pyrotechnic strobe compositions, in which he successfully attributed the behavior to alternating 'dark' and 'flash' reactions, each resulting from the reaction of a different oxidizer-fuel pairing.

In 1992, Jennings-White [4] reported that bismuth (III) oxide could be substituted for the toxic lead compounds to make highly effective crackle, and by that time it had also become a common practice to include a proportion of copper (II) oxide. Since that date, there appears to have been no other published systematic study of pyrotechnic crackle compositions. Instead, a common consensus appears to have arisen in the Western pyrotechnic community that crackle compositions *must* a) contain a 'heavy' metal (usually lead or bismuth) oxide, b) include magnesium (alloyed with aluminum) so that it is available to be preferentially consumed in the 'dark' reaction, and c) be bound with NC (or its close cousin, double-based powder). The few documented compositions [2,4–6] – and the vast majority of more informally published ones – follow these principles.

Of particular note is a formulation that was developed by Lloyd Sponenburgh [7] and is listed in Table 1. For the best performance and timing, he recommends that the composition should be bound and granulated with the aid

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Table 1. Sponenburgh crackle composition [7].

Material	%
Bi ₂ O ₃	71.4
Magnalium, –200 mesh	14.3
CuO	9.5
Al, atomized, –200 mesh	4.8

of an additional 2.6% 'Green Dot' double-based powder, dissolved in acetone, although a similar quantity of NC – again dissolved in acetone – appears to give satisfactory, if not ideal, results. Sponenburgh engineered this composition to be easy to ignite (needing only a thin priming layer of black powder), and to have a short, highly consistent delay and a loud, sharp report. It, together with one or two minor variants, is widely used in both the professional and amateur pyrotechnic communities and is generally considered to be the standard by which other crackle compositions should be judged.

In recent years, environmental concerns have resulted in lead compounds being widely banned as ingredients in commercially available fireworks. As reviewed by Lin [8], concerns are also being raised regarding the environmental impact of particulate matter that is released by fireworks, in terms of both air quality and the resulting contamination of ground- and surface water. Much current pyrotechnic research [9] has, as at least one of its aims, the goal of reducing the dependence on heavy metals and other toxic materials. Thermites offer a relatively non-toxic approach to the production of materials with a wide range of chemical and energetic properties [10].

Several years ago, it became apparent that Chinese manufacturers were producing crackle that contained neither bismuth nor lead. A qualitative analysis of a small sample of a Chinese product revealed that the only significant ingredients in the cores were CuO, Al and Mg. Both the cores and the surface coating of prime – which was a black powder composition with added magnalium – were bound with a highly cured phenol-based resin. Attempts to reproduce the effect led to the development of a number of novel relatively simple but effective crackle formulations [11–14].

Further investigation, aimed at simplifying the composition as much as possible, eventually led to a previously unpublished crackle formulation, shown in Table 2, containing only copper (II) oxide and atomized aluminum in closely stoichiometric proportions, plus a small percentage of phe-

nol formaldehyde (phenolic resin) as the binder. The present study aims at understanding the mechanism (or mechanisms) at work in such a chemically simple, but effective, pyrotechnic crackle composition.

Considerable work has been undertaken over the last decade into the reaction mechanisms of nano-thermite systems, particularly mixtures of Al and CuO [15–20]. It is generally accepted that in such nanothermite systems, a key parameter to high reactivity is intimate contact between the fuel and oxidizer [21]. In consequence, research has also concentrated on the nature of the interface and techniques by means of which such contact might be enhanced [22–25].

Although the dependence of propagation and ignition on both fuel and oxidizer particle sizes has been investigated to some extent [26,27], there currently appears to be little understanding of the degree to which the findings from nanothermite research might also apply to thermite mixtures that are composed solely of micron-sized particles.

2 Experimental Section

2.1 Apparatus

A small Type G thermocouple, embedded in a primed crackle grain, measured the grain's internal temperature as the reaction proceeds from ignition to explosion. The thermocouple was connected to a DC amplifier that had three outputs, with overall gains of 100, 200 and 400 respectively. The outputs were connected to three of the analogue inputs of an Arduino Uno, which performed the A/D conversions and transmitted the data, via a Bluetooth link, to a Raspberry Pi that ran the controlling software and wrote the data to file, for later analysis.

The recording software performed the voltage to temperature conversion with the aid of published tabular data [28] and the conversion was checked by calibration at the temperature of melting KNO₃ (607 K). The calibration results indicated that the measured temperatures are likely to have an inaccuracy of no more than 10 K. Recording all three channels means that there is good resolution on one channel or another over the whole measurable temperature range, from ambient to 3040 K, and also provides a good indicator of the internal consistency of the measurements in the mid-temperature range, where all three channels give a meaningful output.

The length of time over which data was collected is selectable from a range of values between 5 and 60 seconds, and at intervals that are again selectable to lie between 1 and 20 milliseconds. The longer recording and interval times were used for calibration runs; all the data described here was recorded over a 10 second period, at 1 ms intervals.

Each thermocouple was constructed as a 5-turn twisted pair from 0.1 mm diameter tungsten (+ve) and tungsten-

Table 2. Crackle composition.

Material	%
CuO –300 mesh	81
Al, atomized, –350 mesh	19
Phenolic resin	+3

rhodium alloy (26 wt% Re) wires. Their small size means that their effective mass (around 2% of the mass of a typical crackle grain) and their response time (estimated to be much less than the 1 ms interval between measurements) do not appear to cause any significant distortion of the measured temperatures.

Early trials showed the need for two modifications to the construction of the thermocouples. Firstly, in order to obtain consistent readings, it proved necessary to ensure that the point at which the two wires emerge from the twisted pair was embedded as close as possible to the center of the grain. This was made easier by doubling the twisted section back on itself, which also has the advantage of providing a better key for the addition of the crackle compound. More troubling was the observation that there was a tendency for the signal to fall to zero for several tens of milliseconds, just at the point when the explosion was about to occur. It appears that the intensity of the reaction is such that it is capable of temporarily degrading, or even breaking the contact between the twisted wires. Spot welding a point on the twisted pair junction was found to be an effective means of largely eliminating this mode of failure. However, the small diameter and high melting point of the wires means that in a few cases the weld subsequently failed.

Each trial was recorded, using a Panasonic HC-X900 video camera, operating at 25 fps. The camera was positioned at a fixed distance of 3 m, with the audio automatic gain control disabled and the recording level set to –6 dB. An LED, placed in the camera's field of view and triggered by the recording software, enabled the video, audio and temperature records to be synchronized to an accuracy of one video frame (40 ms).

2.2 Sample Preparation

The crackle composition that was used in this study is shown in Table 2. The copper oxide was of 98% purity and specified as passing an approximately 300 mesh screen, with a claimed particle size of less than 54 μm . Under $\times 1000$ 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, which nominally passed 350 mesh, 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.

After thoroughly mixing the copper oxide and aluminum, a weighed quantity of a solution (25 wt% in isopropyl alcohol) of the resin was added. More alcohol was added until a slurry of a suitable thickness was formed. Weighed thermocouples were dipped in the slurry and then left to dry. This process was repeated until the grains had grown to be approximately 3 mm in diameter. The dried thermo-

Table 3. Priming composition.

Material	%
KNO ₃	45
Magnesium, –350 mesh	15
CPVC	12
Charcoal, airfloat	9
Fe ₃ O ₄	9
Sulfur	6
Dextrin	4

couple assemblies were reweighed and photographed so that each grain's mass and precise diameter was known.

The grains were then repeatedly dipped in a water-based slurry of the prime shown in Table 3 until they approached 5 mm in diameter, so that the prime layer was approximately 1 mm thick. Reweighing and re-photographing the completed assemblies allowed the mass and thickness of the prime layer to be calculated. This prime, which was ignited by means of a hand-held blowtorch, was designed to produce a hot slag that quickly and efficiently transfers heat to the crackle core. It appears to work equally well if polyvinyl chloride (PVC), or Parlon, is used instead of chlorinated PVC (CPVC), and if Fe₂O₃ is substituted for the Fe₃O₄.

3 Results and Discussion

The use of an essentially pyrotechnic experimental method resulted in a wide intrinsic variability in the measured data. In particular, the detailed progress of the prime's ignition varied significantly from sample to sample, and the use of very thin thermocouple wires in such a highly energetic environment meant that not all measurement runs were successful. The method used to prepare the samples resulted in relatively poor control of the grains' diameters (from 2.6 to 4.4 mm) and masses (from 50 to 130 mg) and their coating of prime. The performance of this composition is very sensitive to variations in the size of the grains, which should ideally have diameters in the range of 2.5 to 3.0 mm. It is therefore likely that this lack of control contributed to the failure of some of the grains to explode. However, the density of the grains, calculated from their measured mass and diameter, proved to be consistently close to 50% of the theoretical maximum density (TMD).

Table 4 summarizes the sample sets on which the results are based. Set A used thermocouples that were made without the two modifications described in the Experimental Section, meaning that the data was reliable only at temperatures of about 1000 K or lower, and where the temperature was changing relatively slowly. Sets B and C used modified thermocouples and so, in principle, provided valid data over the full temperature range. The total failure of one sample from set C was the result of the thermocouple being destroyed while the prime was still burning; the remaining

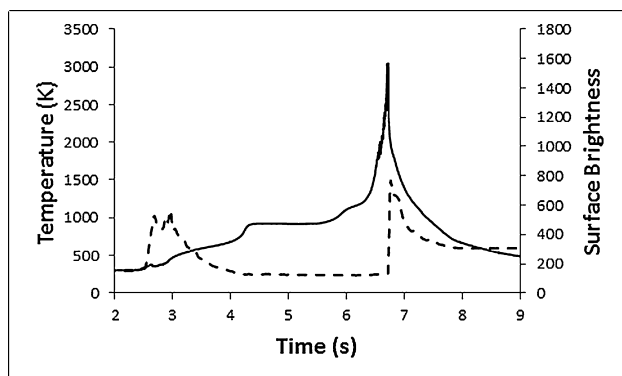
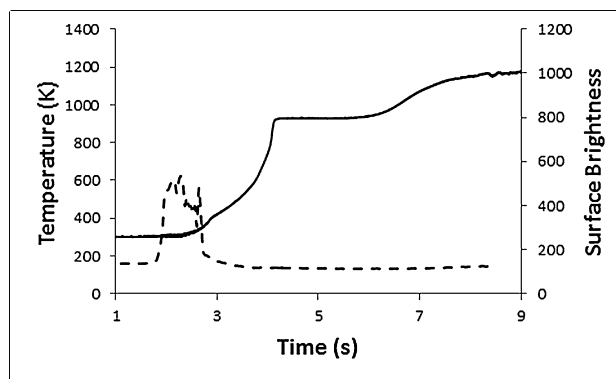
Table 4. Sample summary.

Set ID	Number	Partial failures	Total failures
A	5	0	0
B	5	3	0
C	10	5	1

partial failures were the result either of the grain's failure to explode or because of a temporary anomalous drop in output from the thermocouple. Nineteen samples provided data in the temperature range from ambient to around 1000 K but only six samples gave uninterrupted data across the entire temperature range, from ignition to explosion.

The interpretation of the data depends on the assumption that the thermocouples give readings that are broadly representative of the temperature throughout the grains. The validity of this assumption is supported by results from a simple computer model of the thermal properties of a grain with 50% of the TMD, which indicates that the time taken for temperatures to equalize across a typical grain is about 30 ms. At a representative heating rate of 2000 K s^{-1} , that suggests that – even if heat is being generated highly asymmetrically – the temperature at different points within a grain will not vary by more than about 60 K. Given that internal reactions would be expected to generate heat relatively uniformly, it seems likely that the temperature differences from one point in a grain to another will be significantly less than this value. However, this assumption may not apply when the temperature is changing most rapidly, such as during the transition to the explosive phase. This may, at least in part, account for the variability of the measured temperatures in this region.

Figure 1 shows a typical temperature profile of an ignited sample. The superimposed dotted line represents the surface brightness of the primed grain. This is a dimensionless number, calculated by averaging the sum of the red (R) green (G) and blue (B) channels over a 3×3 square of pixels at the center of the grain's image on each successive frame

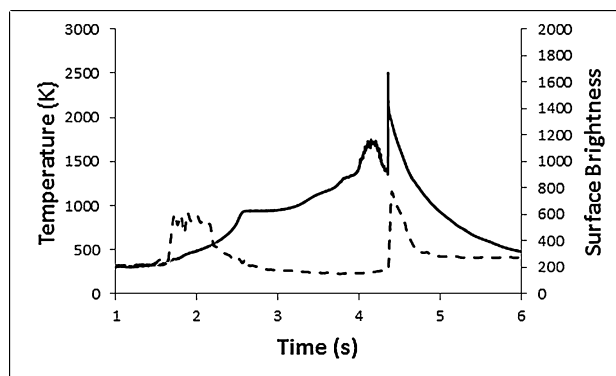
**Figure 1.** Variation of a grain's temperature (solid line) and surface brightness (dotted line) with time.**Figure 2.** Variation of a grain's temperature (solid line) and surface brightness (dotted line) with time, for a sample that failed to explode.

of the simultaneous video recording. Each of the three values has a range of 0 to 255 so that an R+G+B reading of 765 indicates that the image is fully saturated (or over-exposed).

In this case the delay, from the moment of ignition to the explosion, was 4.4 seconds, which is typical for this composition, although there was a degree of variation from sample to sample. A feature that was common to all fully and partially successful runs is the almost step-like rise in temperature from a little above 500 K to just below 1000 K.

Figure 2 shows the temperature profile of a grain that failed to explode. It shows a broadly similar behavior at temperatures up to about 900 K, but at higher temperatures the rate of increase is much slower and the temperature reached a maximum in the region of 1200 K.

Figure 3 shows a case where the measured temperature displays an anomalous dip during the approach to the explosion. This feature was observed to occur, to a greater or lesser degree, in approximately one third of the samples, including those which used spot-welded thermocouples. It is

**Figure 3.** Variation of a grain's temperature (solid line) and surface brightness (dotted line) with time, for a sample showing an anomalous temperature profile.

distinguished from other modes of failure by being of much longer duration, amounting to several tenths of a second, and preceded by a series of small amplitude, high frequency oscillations. It is therefore unlikely to be caused by loss of contact in the twisted pair junction. The onset of the anomaly occurred at any temperature in the range from 1200 to 1800 K and is therefore not likely to be the result of any specific chemical process. A possible cause is conduction between the thermocouple's bare wires by the metal content of the partially reacted mass of thermite. Such a cause would be compatible with the fact that only some samples are affected; it could be critically dependent on the precise geometry of each individual sample.

In all such cases, the thermocouple's output was seen to at least partially recover at the point of explosion, when the grain's material was fully dispersed. There was little or no deposit left on any of the thermocouples after the explosion, and subsequent calibration measurements showed that there was no permanent change in their temperature response. However, the existence of this anomalous behavior means that temperature readings higher than, say, 1200 K must be treated with some degree of caution.

The surface brightness data provides limited information on the behavior of the prime. It suggests that the prime's activity was largely complete within one second from ignition, by which the time the grain's internal temperature had been raised to around 500 K. An earlier trial [29] showed that the prime used in the current study reached a maximum temperature of around 1400 K. There was evidence that very small amounts of energy continued to be generated for several seconds, but that the principal long-term feature was a gradual cooling curve, consistent with a slow loss of heat from the thermally insulating slag. In the current study it is assumed that the prime has no long term effects, other than acting as a thermally insulating layer that reduces heat losses to the surroundings.

A frequency diagram, such as that shown in Figure 4 (based on the same data as is shown in Figure 1) – which plots the number of data points that lie in each 5 degree

temperature interval – reveals a little more information about the process. Since the data is recorded at 1 milli-second intervals, this graph effectively indicates how long the grain's material spent at each temperature. The most significant feature, which appears prominently in the vast majority of the records, is the very strong peak that occurs close to 900 K.

Averaging the measured positions in 17 separate samples gives a value of 932 ± 10 K. It is unlikely that the cause of this feature is anything other than the solid-liquid phase transition of aluminum (at 933 K). Assuming this to be the case, and that the melting aluminum absorbs all the heat being generated from ongoing exothermic reactions (i.e. ignoring factors such as heat loss to the surroundings) it is possible to use the dwell time to estimate the rate at which heat is being generated at this temperature. Although varying somewhat from case to case, all the calculated values lie between 0.05 and 0.2 kW per gram of crackle composition.

The significance of the more complex, low-temperature feature is shown more clearly when the data of Figure 4 is converted into an estimate of the rate at which the temperature changes, as shown in Figure 5.

The detailed behavior varied significantly from sample to sample, but generally included a chaotic region at temperatures below 450 K, followed by a more coherent, steady rise at temperatures above 500 K. The two regions were frequently separated by a more or less pronounced dip in the region of 450 to 500 K. Matching the results for each sample with the corresponding surface brightness data suggests that the initial chaotic region is the result of the core being heated by the irregularly burning prime, but that the steady rise is likely to mark the start of an internal exothermic reaction. When present, the dip at around 500 K appears to mark the transition from one process to the other.

The derivation of the data plotted in Figure 5, effectively being the inverse of integer values that have very small values over much of the temperature range, means that the values have little physical significance except when the temperature is changing relatively slowly, which is why the

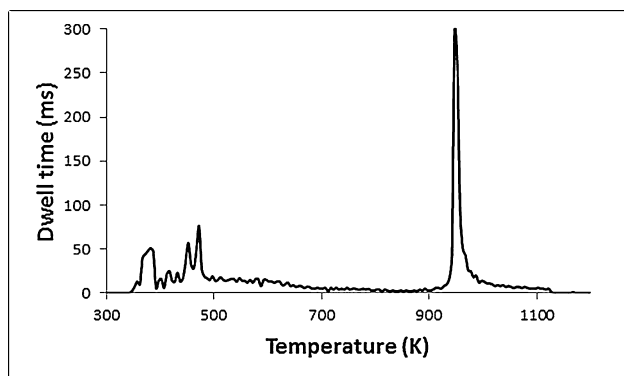


Figure 4. Dwell time in each 5 K temperature interval, derived from the data of Figure 1.

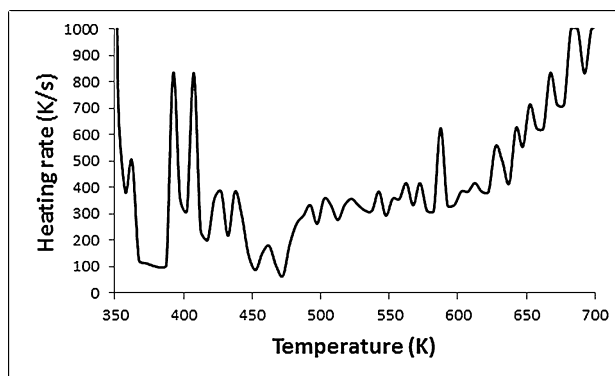


Figure 5. Variation of heating rate with temperature, derived from the data of Figure 4.

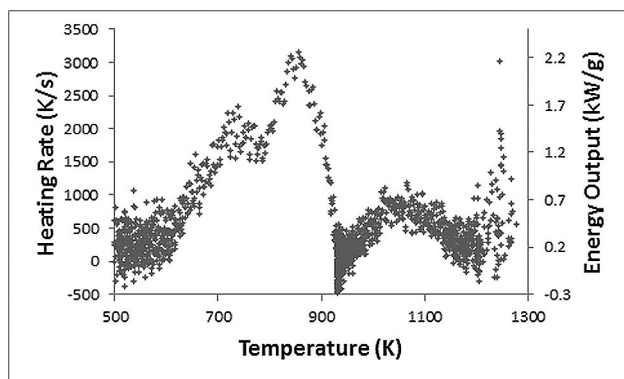


Figure 6. Variation of the rate of heating with temperature, and the corresponding estimated rate of energy generation.

data shown in Figure 5 only extends to a temperature of 700 K. A more meaningful approach, that is equally valid over the whole temperature range, is to evaluate the heating rate directly from the raw temperature data, as shown in Figure 6.

The change in temperature is also used to calculate an estimate of how much energy has to be generated to cause that rise. The calculation applies corrections for the energy lost to the surroundings, estimated from the cooling curves of prime-coated inert grains, and for the estimated variation of the average heat capacity that results from changes in the chemical composition as the reactions progress. Both of these corrections turn out to be relatively small; they tend to act in opposite directions and rarely exceed a few percent of the total. The calculated values give the energy that needs to be generated in each one millisecond time interval and, in order to allow comparison between grains of differing sizes, is expressed as a value per unit mass. For any particular sample, given the smallness of the corrections that are applied, the two ordinate axis scales effectively differ only by a multiplicative factor.

The example shown in Figure 6 has been selected as one that illustrates all the significant features. As explained below, one of these features is not visible in every dataset. In agreement with the simpler analysis shown in Figure 5, the results indicate that there is measurable internal exothermic activity at temperatures as low as 500 K. Thermite reactions at such low temperatures are normally only found in studies of nanocomposites [15]. As reported by Ilunga et al. [30], micron-sized Al–CuO thermites have generally been found difficult to ignite. They quote a typical ignition temperature of 940 °C (1213 K) and discuss the use of additives to improve the ignition and combustion properties.

The observed exothermic activity increases significantly as the temperature reaches about 600 K and an obvious feature in Figure 6 is the broad peak of energy generation between 600 and 900 K, which is present in all cases. As is evidenced by this example, all samples show signs of additional, partially resolved structure in this region.

A closer examination of the feature between 600 and 900 K shows that it always consists of two overlapping components. Figure 7 illustrates that a combination of two Gaussian distributions gives a good fit to the data, and this was found to be the case for all the samples, including those that failed to explode. Note that the decision to use Gaussian curves is not meant to imply anything about the underlying physical processes. It was made on a purely pragmatic basis; on the grounds that the curve is mathematically simple and provides an empirically good fit in all cases.

The lower temperature component is always the broader of the two and it is usually, but not always, the case that the higher temperature component has the larger amplitude. However, the positions of the two components turn out to be remarkably consistent.

The data shows a very sharp minimum at about 930 K, followed by a much slower increase toward higher temperatures. At 933 K, the solid-liquid transition temperature of aluminum, all the chemically generated energy is consumed by the phase change and the calculation of the net energy necessarily gives a result close to zero. Once all the aluminum has melted, the temperature will start to rise again, resulting in a non-zero value for the energy generation. The average calculated value in the temperature range from 940 and 950 K is close to 0.1 kW g⁻¹ which is in good agreement with the earlier estimate (0.05 to 0.2 kW g⁻¹) that was obtained from the measured dwell times. The relatively long dwell time at a temperature close to 933 K, amounting to several tenths of a second, appears to be the result of the coincidence of the melting point of aluminum with a region in which the rate of generation of energy happens to be particularly low.

At higher temperatures the rate of generation of energy rises once more, until there is a sudden – and frequently chaotic – transition to thermal runaway in the explosive phase. This transition is the most unpredictable feature of the data, with the measured temperatures for individual

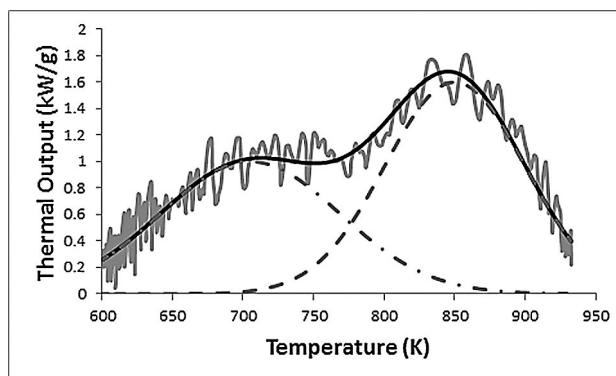


Figure 7. Empirical fit of the sum (solid line) of two Gaussian distributions (dotted lines) with an observed energy-temperature profile.

samples being uniformly spread over the range from 1000 to 1380 K. The extent to which the reaction had progressed at the point of transition was estimated by summing the calculated energies up to that point. As expected, the results also showed a moderately wide spread in values, with the transition occurring when the reaction was between 20% and 36% complete.

In those cases where the transition occurred at a temperature of, say, 1200 K or higher, there was evidence of a further peak of energy generation in the vicinity of 1050 K. The evidence suggests that this third maximum would always be visible were it not for the masking effect of the explosive transition when it occurs at temperatures below 1200 K. In the cases where the position of the 1050 K peak was measurable, the resulting values are also highly consistent.

When the explosive transition occurs at a temperature below 1200 K, it would seem reasonable to infer that the underlying driving reaction is the one associated with the third exothermic feature. However, the existence of cases where the transition takes place at significantly higher temperatures suggests that there may be an additional, fourth exotherm. Although the current data gives no direct evidence for such an exothermic event, there are hints that place limits on its possible position, should it exist. The data of Figure 6 point to its location being at a temperature above 1200 K. Furthermore, the highest temperature recorded in the samples that failed to explode was 1260 K, which imposes a slightly greater lower limit. An estimate of an upper limit is the maximum observed temperature at which the explosive transition occurred, at 1380 K.

The temperatures for the three measured exothermic features, together with the estimated range for the implied fourth are given in the last column of Table 5. Research by Umbrajkar et al. [15] provides support for the interpretation of these exothermic features in terms of distinct modes, or steps, of the overall Al–CuO reaction. The authors investigated the properties and behavior of a closely stoichiometric Al–CuO nanocomposite, using a combination of sophisticated techniques, including scanning electron microscopy (SEM), X-ray diffraction analysis and differential scanning calorimetry (DSC). Their analysis of the DSC results showed the existence of four reaction steps that occurred over four different, but overlapping temperature ranges and they were able to determine the activation energy and

reaction type for each step. Their measured ranges and the corresponding midpoints are shown in the second and third columns of Table 5.

In their discussion, the authors expressed the opinion that, although individual parameters such as the frequency factors will be specific for the morphology of each particular sample, the overall reaction mechanism is expected to remain valid for any Al–CuO composite. At first sight, it is clear that the crackle exotherm temperatures are significantly higher than the corresponding midpoint temperatures in Table 5. However, such a discrepancy might be expected to occur. Umbrajkar et al.'s results came from DSC measurements on a nanocomposite, with externally applied heat and a heating rate of 5 K min^{−1} (0.083 K s^{−1}). They noted that in hot wire ignition tests, with a greater heating rate (about 1000 K s^{−1}) but on the same materials, the stronger exothermic events occurred at “much higher temperatures”. For a composite with much larger particle sizes, and with internal energy generation that causes a heating rate that is typically in the region of 2000 K s^{−1}, it is not unreasonable to expect that a similar shift might occur. Figure 8 shows that there is excellent correlation between the two sets of data. The straight line is the best fit (with $R^2 = 0.998$) to the first three temperatures; the superimposed fourth point has an ordinate and error bars that are derived from the estimates given earlier.

Umbrajkar et al. also made DSC recordings at a range of different heating rates and were able to observe how that affected the positions of the peaks for their four reaction steps. The values derived from their results are plotted in Figure 9. For all four steps, their data shows a consistent relationship between their positions and the heating rate. In all four cases there is a good fit between their results and the open symbols that represent values measured in the current study.

If this correspondence is taken to be significant, then it seems likely that the lower temperature reaction mechanisms in the crackle composition do not greatly differ from

Table 5. Approximate temperature ranges and their midpoints (columns 2 and 3) for Umbrajkar et al.'s [15] four reaction steps, and the observed corresponding crackle exotherm temperatures.

Step No.	Range (K)	Midpoint (K)	Crackle Exotherms (K)
1	350–550	450	718 ± 20
2	450–650	550	840 ± 20
3	600–800	700	1057 ± 25
4	850–1000	925	1260–1380

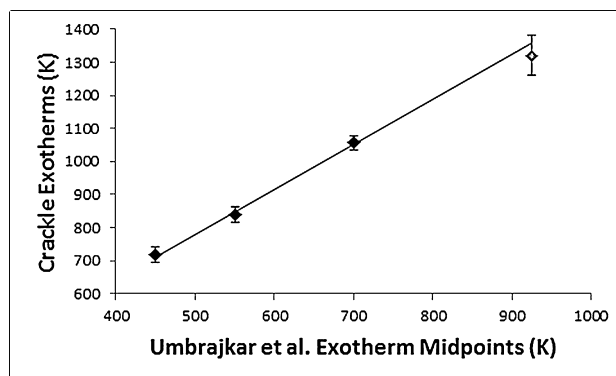


Figure 8. Correlation of the crackle composition's measured exothermic event temperatures with the mean positions reported by Umbrajkar et al. [15].

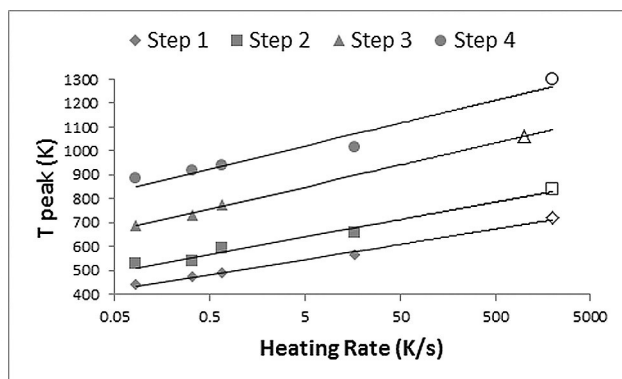


Figure 9. The variation of the peak temperature of the four reaction steps with heating rate, taken from Umbrajkar et al. [15]. The open symbols represent the corresponding data from the current study. Note that the horizontal axis scale is logarithmic.

the ones that Umbrajkar et al. propose; that is, by (partial) decomposition of CuO, followed by diffusion of the reacting species, limited by the growth of intervening layers of amorphous or crystalline Al_2O_3 .

One problem with that identification is that Umbrajkar et al. found their third exotherm to be of greater amplitude than the first two, whereas the opposite is true for the crackle composition. However, theoretical studies of the reaction mechanism [16, 17, 23] indicate that the particle interface, and the nature and initial thickness of the Al_2O_3 layer are likely to play a crucial role in determining the reaction kinetics. Furthermore, experimental data [25, 26, 27] demonstrates that nanocomposites which are constructed by different means or with particles of different sizes show significant differences in the way that the reaction progresses. Given the large morphological differences between the crackle composition and a nanocomposite, a detailed match between their behaviors is not to be expected.

The results of this investigation give relatively limited information regarding the nature of the transition to the ex-

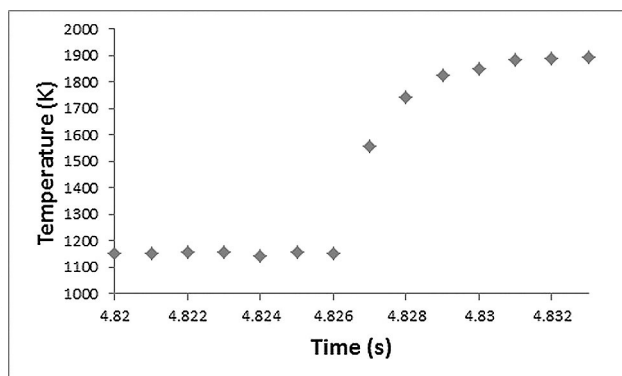


Figure 10. The temperature change associated with the onset of the explosive phase. The heating rate can approach $4 \times 10^5 \text{ K s}^{-1}$.

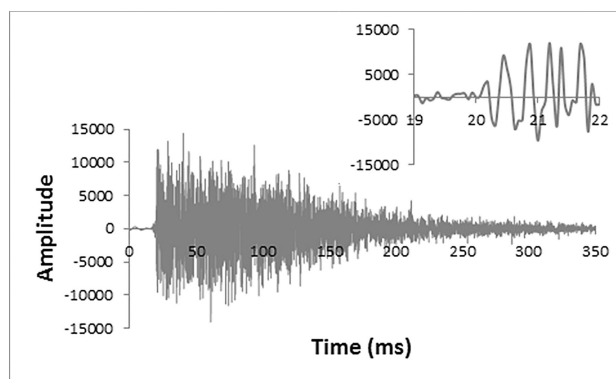


Figure 11. Audio recording of a crackle grain report. Inset is a detailed view of the rise in amplitude over the three millisecond period around the start of the explosion.

plosive phase. As illustrated in Figure 10, the transition is marked by a sudden increase in the temperature. The measured peak temperature was typically around 2000 K or above, but in some cases briefly exceeded the 3040 K limit imposed by the apparatus. The observed range of peak temperatures is in moderately good agreement with theoretical calculations [18] and broadly brackets both the pyrometrically determined values found for Al–CuO nanothermite by Weissmiller et al. [30] and those measured by means of NIR spectrometry for micron-sized mixtures by Knapp et al. [31].

Simultaneous audio recordings, such as the one shown in Figure 11, indicate that there was a correspondingly sudden rise in amplitude, taking no more than 0.5 to 1 ms, followed by a slow decay that lasted for a few tenths of a second. The length of the decay period implies that the reaction takes place over an extended period of time, rather than involving the whole grain in the same instant.

That interpretation is supported by video images such as that shown in Figure 12, which indicates that some of the material that has been ejected from the exploding grain can itself later undergo an energetic reaction. Weissmiller



Figure 12. Video frame taken approximately 80 ms after the start of an explosion, illustrating the ejection of unreacted material.

et al. [30] found corresponding extended burn times – admittedly on the significantly shorter timescale of the order of 1000 μ s – in their burn tube measurements of Al–CuO nanothermite.

The sudden onset of the explosive phase suggests that it occurs as the result of the reactants being driven into a critical state by the energy released in one of the underlying, more orderly exothermic reaction stages, resulting in a dramatic increase in the rate of gas production. It takes place at a temperature that significantly exceeds the melting point of aluminum and may, therefore, be a consequence of more intimate mixing of the reactants. It has been suggested [27] that rapid sintering may negate the reactive advantage that nano-sized oxidizers have over those with larger particle dimensions and [21,25] that gas generation from an NC binder improves the performance of nanocomposites, either by preventing the occurrence of sintering or by enhancing heat transfer. In the present case, with both oxidizer and fuel particles being micron-sized, it is unclear what part sintering, or the effect of gaseous products from the decomposition of the phenolic resin binder, play in the transition.

Comparisons between the current findings and those of other researchers are made more difficult by the differences in both the morphology of the materials used and the experimental techniques. Apart from the fact that the published research into Al–CuO thermites deals almost exclusively with mixtures where at least one, and usually both, the initial reactants are composed of nano-sized particles, investigations of propagation rates, and particularly of gas production, are generally performed in a partially confined [25,26] or fully confined [20–22,27,33] environment. Despite the fact that the crackle grains were essentially unconfined, the observed rise time of the audio recordings is in excellent agreement with the 0.75 ± 0.1 ms pressure rise time measured by Egan et al. [27] for a mix of nano-Al and micron-CuO.

Initial, approximate modelling of the Al–CuO reaction by Bajot et al. [18] gave results which they claim, despite differences of detail, show a fair overall agreement with experimental data. Their calculations indicated that, for a sample with 50% TMD, the peak pressure is attained when the reaction is 50% complete. Given the uncertainties, in both their model and the current study, that seems to be in fair agreement with the observation that the crackle composition's explosive transition took place when the reaction was $28 \pm 8\%$ complete. Later work by some of the same authors [19], using a more refined model, indicated that the onset of significant gas production will be very abrupt, a conclusion that is in at least qualitative agreement with the findings of this study and of the experimental results obtained by other researchers [33,26].

The measurements of the temperature at which the transition to the explosive phase takes place, and the maximum temperature during the explosion, both show a fairly wide spread of values. This might be a result of conductive

material disrupting the thermocouple's response, as discussed earlier. Even if this does not occur, the observed chaotic behavior around the point at which the transition begins, together with the audio and video evidence discussed earlier, might indicate that it is initiated in one or more highly localized hot-spots whose temperature, depending on their precise location, might not be recorded by the thermocouple. Similar considerations might also apply to the peak temperatures, bearing in mind the rapidity of the temperature rise and the fact that the grain's material is violently dispersed by the explosive reaction. In either case, the highest measured temperatures – around 1380 K for the transition, and greater than 3040 K for the temperature of the exploding material – might be more representative of the physical state. A temperature in excess of 3000 K is certainly more in line with theoretical predictions [19] of the temperature at which gas production is likely to become significant.

In contrast, the progress of the interaction from ignition to beyond the melting point of aluminum appears to be well characterized by the highly consistent results over that range, across all the sample sets. That consistency provides a well-defined behavioral baseline for future research into more complex crackle compositions. By observing the differences in behavior that result from the inclusion of other commonly used materials, such as magnalium and bismuth (III) oxide, it may be possible to infer what part they play in the progress of the reactions.

4 Conclusions

Despite the issues that result in a degree of inconsistency of the thermocouple measurements at higher temperatures, this study demonstrates that simple techniques, using relatively inexpensive apparatus, are capable of revealing many of the features of the crackle reaction. The composition given in Table 2 has to be one of the simplest mixtures that can produce the pyrotechnic crackle effect. Compared with the more commonly used, more chemically complex compositions, such as that given in Table 1, it is much more sensitive to variations in the grain size, significantly harder to ignite, has a longer and more variable delay and is much less consistent in terms of the loudness and sharpness of the report. The Chinese compositions, which contain magnalium but no lead or bismuth oxide, appear to exhibit properties that are, in all respects, intermediate between those of the two compositional extremes listed in Tables 1 and 2. Although the present two-component formulation is unlikely to replace any of the ones currently in use by either amateur or professional pyrotechnicians, its very simplicity has allowed some of the details of the combustion mechanism to be revealed.

This study shows that the reaction becomes self-sustaining at temperatures as low as 500 K, which is much lower than the generally accepted ignition temperature of ther-

mites composed of micron-sized particles. It progresses by means of at least three – and probably four – steps, the first two of which, together with the melting of the aluminum, give rise to the bulk of the delay (or, in Shimizu's [2] terms, the dark reaction). In the absence of magnesium, the 'surface oxidizing reaction of the aluminum particles' is the only one of Shimizu's hypotheses that can apply to the composition of Table 2. While it is possible that 'an oxidizing reaction of magnesium in the magnalium alloy' might play a role in other crackle compositions, the results of this study demonstrate that it is not the only mechanism that can give rise to the crackle effect.

Comparison of the observed behavior with existing experimental and theoretical investigations of Al–CuO nanocomposites reveals a number of intriguing parallels, though frequently at different temperatures and on different time-scales. The most notable of these is the existence of a series of reaction steps, where there is a remarkably good correlation with previous findings [15], whose underlying mechanisms have been investigated [16, 17].

Partly because of the less reliable temperature measurements, but also because of the nature and speed of the reaction at that point, the transition to the explosive phase is less well characterized. However, it appears to be driven by the third or fourth step of the underlying, more orderly exothermic reaction. The transition is very abrupt, being accompanied by a rapid rise in temperature and a sudden increase in the generation of gaseous products. The observed behavior shows a broad, qualitative agreement with findings of nanothermite research, from both the experimental [22, 26, 33] and theoretical [19] points of view.

Irrespective of any interpretation in terms of the chemical mechanism, the results of this study provide a baseline for the investigation of more complex crackle compositions. Future work will focus on examining how the behavior is modified by the introduction of magnalium and/or bismuth (III) oxide.

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