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ABSTRACT

Electric matches are used in pyrotechnics to initiate devices electrically rather than by burning fuses. Fuses have the disadvantage of burning with a long delay before igniting a pyrotechnic device, while electric matches can instantaneously fire a device at a user's command. In addition, electric matches can be fired remotely at a safe distance. Unfortunately, most current commercial electric match compositions contain lead as thiocyanate, nitroresorcinate or tetroxide, which when burned, produces lead-containing smoke. This lead pollutant presents environmental exposure problems to cast, crew, and audience. The reason that these lead containing compounds are used as electric match compositions is that these mixtures have the required thermal stability, yet are simultaneously able to be initiated reliably by a very small thermal stimulus. A possible alternative to lead-containing compounds is nanoscale thermite materials (metastable intermolecular composites or MIC). These superthermite materials can be formulated to be extremely spark sensitive with tunable reaction rate and yield high temperature products. We have formulated and manufactured lead-free electric matches based on nanoscale Al/MoO_3 mixtures. We have determined that these matches fire reliably and to consistently ignite a sample of black powder. Initial safety, ageing and performance results are presented in this paper.

INTRODUCTION

A commercial electric match head consists of an electrically insulating substrate with copper foil cladding, similar to that used for printed circuit boards. A schematic of a typical electric match is illustrated in Fig. 1. Soldered across the edge of the match is a small diameter nichrome wire. This bare match head is dipped into lead-based compositions to produce the spark-sensitive bead above the nichrome bridge wire. The bead may be coated with a second layer of metal fuels such as aluminum/magnesium alloy or titanium with potassium perchlorate oxidizer. This secondary coat provides the hot sparks to ignite black powder (or other compositions) in pyrotechnic devices. Finally the bead may be coated with a

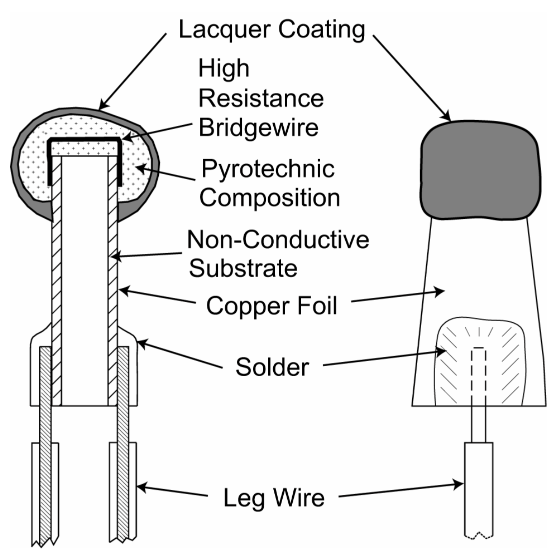

Figure 1. Illustration of a typical electric match in cross-section (left) and viewed externally after rotating 90° (right). [1]

lacquer to provide strength and water resistance.

Unfortunately, most current commercial electric match compositions contain lead in the form of thiocyanate, nitroresorcinate or tetroxide, which when burned, produces lead-containing smoke. This pollutant presents possible environmental exposure and contamination of firing areas.

Finding a lead-free substitute with the appropriate ignition properties is particularly difficult, however, metastable intermolecular composite (MIC) materials, such as nanoscale Al/MoO_3 superthermites, can be remarkably sensitive to small thermal stimuli yet do not contain lead. Thermite mixtures have high heats of reactions and produce high temperature products.[2] Further, the reaction rate is very rapid for nanoscale thermites and can be tuned by the particle size.[3-5] In this paper we present the methods developed to make lead free electric matches, as well as the initial performance and safety evaluation results. Additional performance and safety evaluations are being performed currently and those results will be presented elsewhere.

MANUFACTURE OF MIC-BASED ELECTRIC MATCHES

Materials Used

Figure 2 is a scanning electron micrograph (SEM) of Technanogy nanoaluminum, which is designated as Technanogy 40 nm aluminum. As seen in the figure, the size distribution is reasonably narrow near 40 nm. Larger sized material tends to have a broader size distribution. This is illustrated in Fig. 3 for material designated Technanogy 121 nm aluminum, where particles as large as 1 micron are seen. We also used a similar material obtained from Techanogy, denoted Techanogy 132 nm aluminum. This broad distribution may be desirable in some applications, as appears to be the case for electric matches.

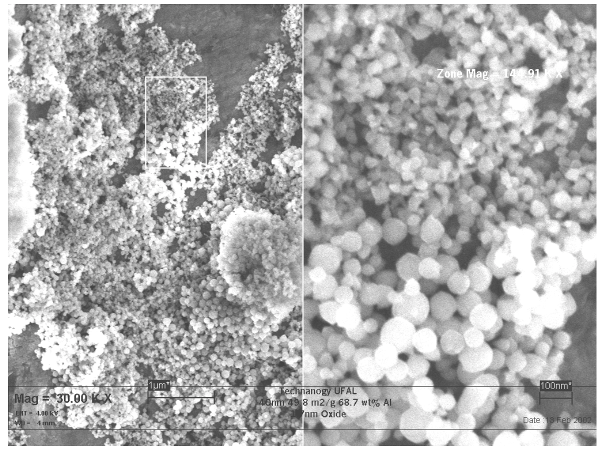

Figure 2. SEM of "40 nm" Technanogy Aluminum.

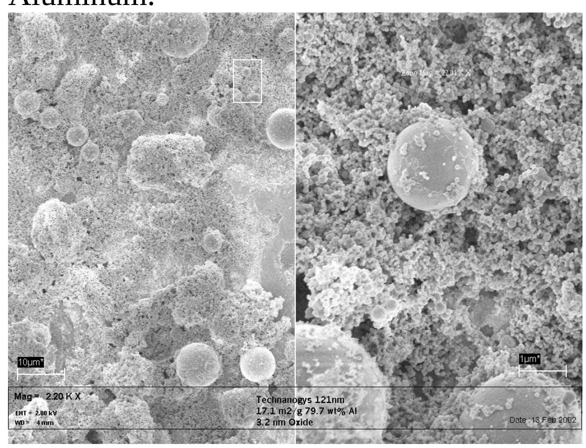

Figure 3. SEM of "121 nm" Technanogy Aluminum.

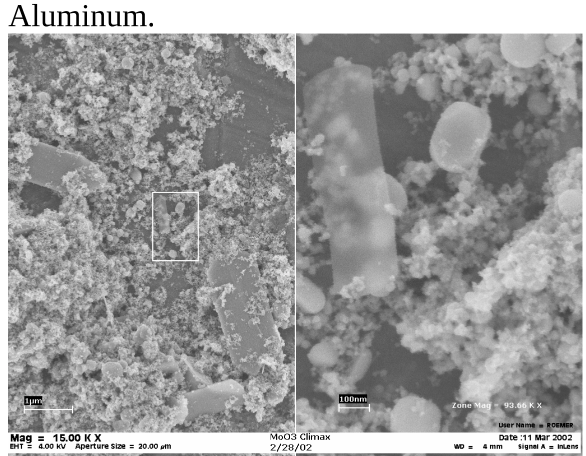

Figure 4. SEM of Climax MoO_3.

The MIC oxidant is nano-scale MoO_3 obtained from Climax Corporation. As shown in Fig. 4, this material is in the form of flakes and smaller agglomerates. From small-angle scattering, the thickness of the flakes is approximately 15 nm. Peterson *et al.* provides details concerning the small-angle scattering technique.[6]

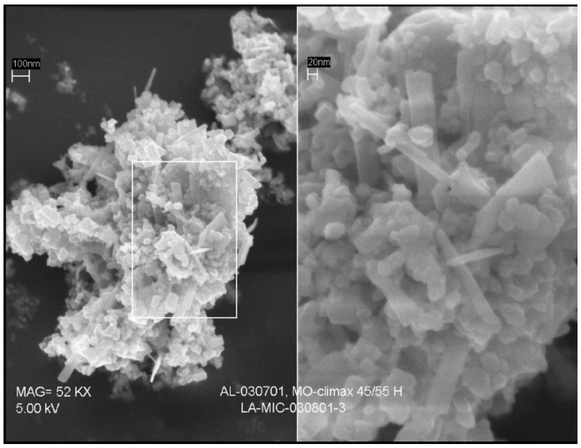

Figure 5. Typical Al/MoO_3 MIC.

By sonically mixing these ingredients we obtain a superthermite. An example of the resulting mixture is shown in Fig. 5. In the figure shown, small nano-aluminum (~40 nm) is used.

Formulation of Match Materials

A bare electric match (i.e. a match head with no bead of composition) is effective in igniting a MIC mixture. However that alone, or even with a simple binder, is not an adequate configuration as we determined through various iterations. Our latest match system consists of three layers. The primary layer is mainly MIC; the secondary is composed of material to provide large ignition particles; and the final layer is a protective coating to provide mechanical strength and keep oxygen and moisture out of the match. The latest formulation used is described here.

The primary layer consists of about 6 mg of a mixture composed of 9% by weight of 13.5% N content nitrocellulose (NC) and 91% of a mixture of 121 nm and 132 nm Techanogy Aluminum based MIC. The bare electric match head is dipped into the composition that has been diluted/dissolved with ethyl acetate containing 0.3% FC 430 surfactant. To provide a barrier the primary dip is coated with NC using a NC/ethyl acetate lacquer.

The secondary dip material is composed of 56% by weight potassium perchlorate, finely ground, 27% 12 micron German Black aluminum, 8% Ti (80-100 mesh), 0.3% Nanocat iron oxide from Mach I, 8.7% NC and enough ethyl acetate solvent to form a viscous slurry. The match is dipped into this secondary material, followed again by a protective coat of NC using NC/ethyl acetate lacquer. The final coat is vinyl dissolved in MEK/Toluene. This procedure has been modified several times and will likely be modified further. Some example matches are shown in Fig. 6. Reasonable uniformity is obtained and the match head is reasonably strong mechanically.

Figure 6. MIC-based electric matches.

AGEING ISSUES

An issue that must be addressed for nano-aluminum is "ageing". Specifically, when exposed to oxygen or water nano-aluminum fully oxidizes making the material useless. A reason the final coating of vinyl was used is to provide a water resistant coating. The electric matches continued to perform even after three weeks submerged in water. Additionally, we have tested matches using fluorosilane coated nano-aluminum. This provides additional protection of the aluminum and the matches appear to perform adequately also.

PRELIMINARY SAFETY TESTS

An initial impact test was performed. Impacts at 55 cm resulted in no reaction, however at 60 cm some ignited. For comparison, a Martinez E-Max-Minimatch achieved ignition at 10 and 13 cm on the Los Alamos drop impact test (2.5 kg weight bare anvil).

We also placed two of the MIC matches towards each other and fired one of the matches. The firing of the first match failed to ignite the second match. MIC typically has good thermal sensitivity.

Our safety and performance testing at Los Alamos is focused on explosives. Consequently, our testing equipment, for friction and spark, is not appropriate for electric matches. Ken Kosanke of Pyrolabs has agreed to test our electric matches. Kosanke has agreed to perform impact, impact with black powder, ESD (electrostatic discharge) through bridgewire, ESD through composition, coating resistance, friction, friction with black powder, thermal sensitivity, ramp firing current, and thermal output tests. We will report these results elsewhere.

MATCH PERFORMANCE

Our initial MIC-based matches were made with Technanogy 40 nm MIC. The electrical spark was adequate to ignite the match consistently but reacted so violently that it sometimes failed to ignite unconfined black powder. Consequently, we changed our formulation to use the larger nano-aluminum and consistent ignition of black powder was obtained.

A qualitative comparison was made by comparing high-speed video records of Martinez Minimatches and our lead-free matches. Figures 7 & 8 shows this comparison. The scale of the view is approximately 12 inches. Figure 9 is a close up view of a MIC-based match igniting. As shown the MIC-based matches react faster (more explosively) than the Martinez match. The hot particles are propelled at least as far as the commercial match. The exposure of the camera is the same for the two image sets. The MIC-based match is brighter than the commercial match, which may indicate hotter products. Further modification of the formulation could likely slow the reaction, if desired.

SUMMARY

Lead-free electric matches have been developed and demonstrated. Further evaluation is proceeding. However, performance appears to be good and initial safety evaluation appears adequate.

ACKNOWLEDGEMENTS

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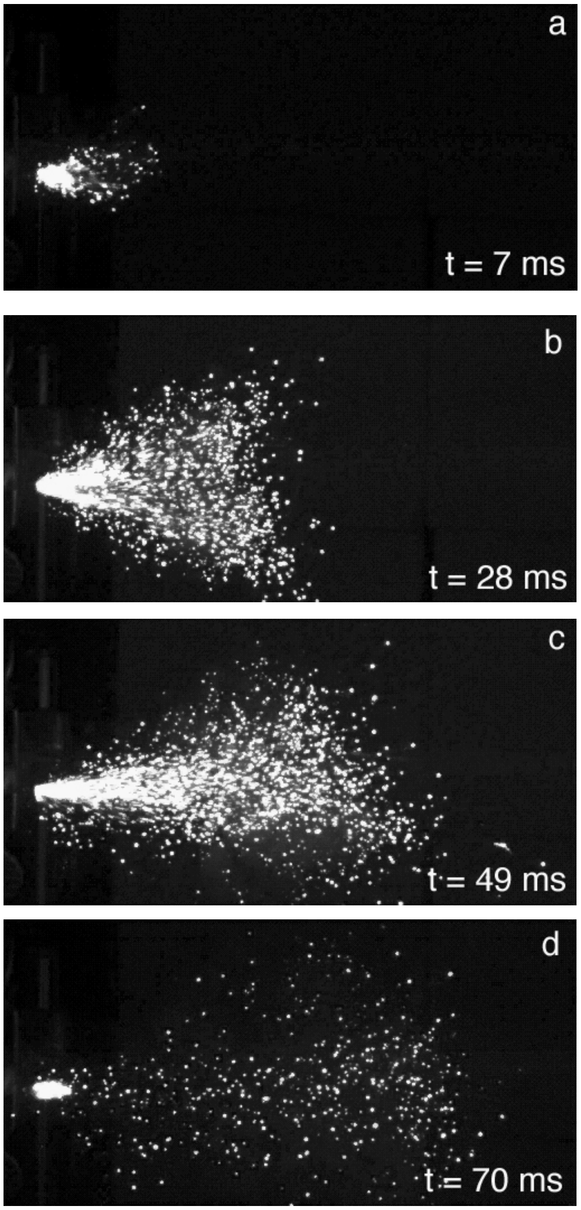

Figure 7. High-speed video of a Martinez Minimatch. Time is relative to first light.

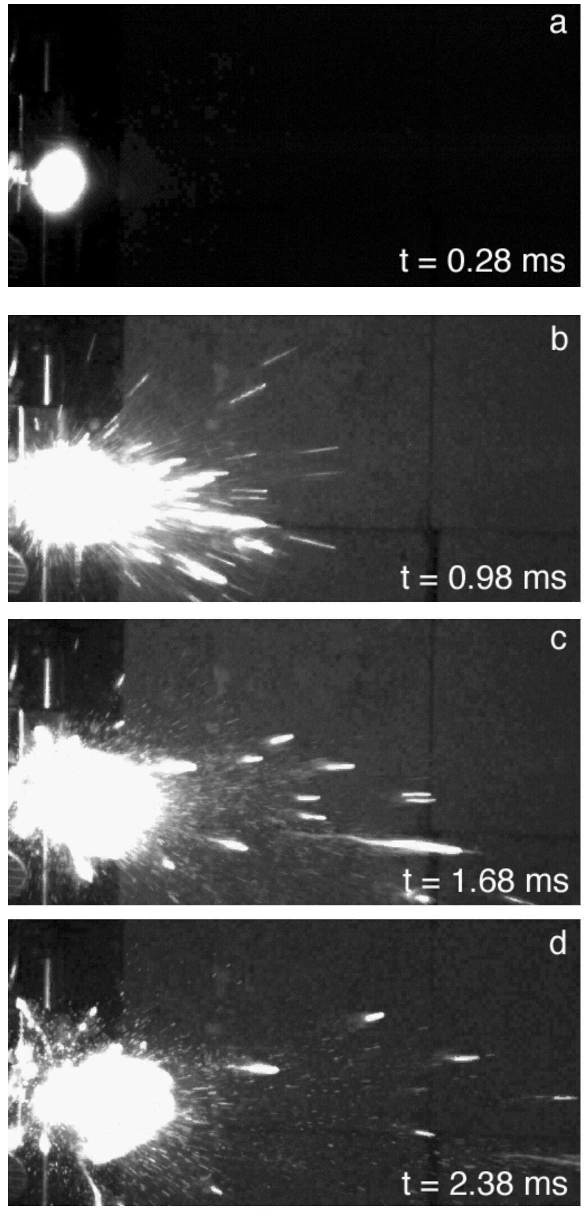

Figure 8. High-speed video of a lead-free match. Time is relative to first light.

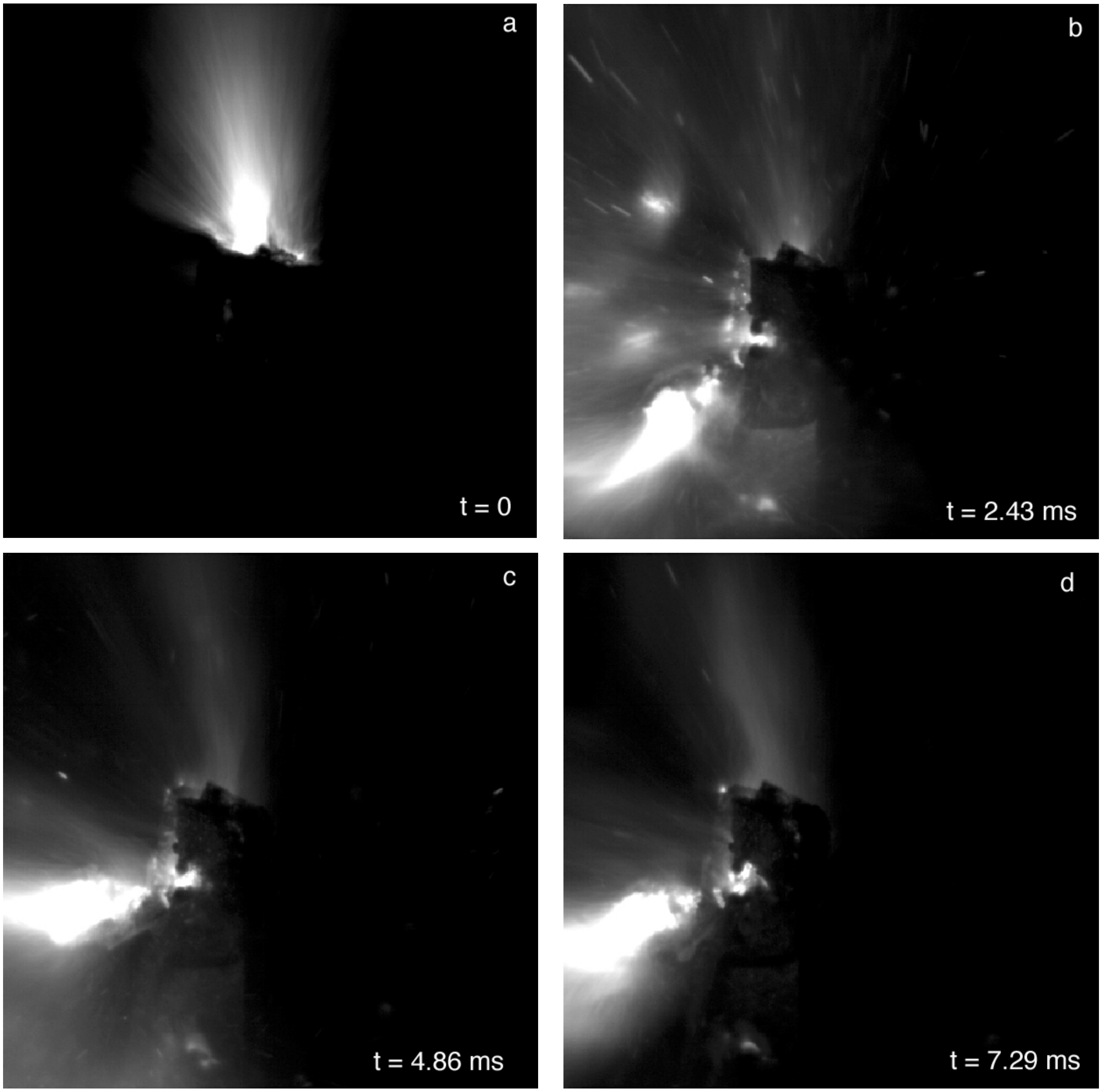

Figure 9. Close-up high speed video of a lead-free match. Time is relative to first light.