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Subject: Zinc-Aluminum Alloy Dust Issues
Literature Search Report and Experimental Summary

Executive Summary

Transmet Corporation produces a zinc-4% aluminum alloy metal shot product that offers superior performance in certain metal cleaning (shot blasting) applications. The hazards of handling pure aluminum dust or fine particulate are well known in industry. Consequently, some concerns were raised whether fine Zn-4Al dust generated as the shot deteriorates by mechanical comminution presents greater flammability or explosivity hazards than other shot blast media.

Transmet contracted Material Technology Innovations, LLC (MTI) to perform a technical literature search to identify whether problems have been experienced by others with zinc-aluminum alloys and to provide recommendations for experimental tests or characterization methods to assess whether such hazards exist.

The technical literature search did not uncover any references citing any greater flammability or explosivity issues peculiar to fine zinc or zinc-aluminum dusts. Numerous references were found to the explosive hazards of pure aluminum due to its highly exothermic heat of formation of the oxide. References noted that alloying aluminum with other elements greatly diminishes its reactivity. A number of references discussed safety issues inherent to fine dusts of many types due to their increased reactivity from their high surface area. No references were found indicating that mechanical comminution can separate Zn-Al alloys into separate elements, which might conceivably increase the hazard of the pure aluminum fraction.

MTI recommended an experiment to Transmet to determine whether separation of the Zn-4Al alloy into separate elements, creating fine pure aluminum dust, might occur during shot blasting. Transmet's Zn-4Al shot was processed in an Ervin Industries Abrasive Test Machine to generate fines. A second batch of Zn-4Al shot was also processed which had been artificially aged to investigate whether its behavior might change over time. The fines from each batch were placed in a graduated cylinder and vibrated using a Ro-Tap device, which would segregate the fines according to density (heavier zinc towards the bottom and lighter aluminum towards the top).

Samples were carefully collected from the upper and lower portions of the cylinder after vibration and were sent to NSL Analytical for chemical analysis. The test results indicated that the aluminum content in the top portion and the bottom portions for both the as-cast shot and the artificially aged shot were virtually identical, indicating that no elemental segregation had occurred.

MTI concluded that Transmet's Zn-4Al shot does not pose a greater risk for fires or explosions from generated fines than other common shot blast media.

Literature Search Strategy

MTI accessed library services at The Ohio State University to perform a technical literature search of the following electronic databases: Academic Search Complete, Scholarly & Reference E-Books, OhioLINK Library Catalog, and the Electronic Journal Center.

The literature search sought to find information related to:

- Incidents of fires or explosions in shot blast cabinets,
- Evidence of de-alloying (separation of zinc and aluminum phases) during mechanical attrition or other deformation typical of shot blasting,
- General information about flammability and explosivity issues for fine metal dust, including effects of particle size, composition, concentration, exposure to humidity, etc.

The search strategy used various combinations of key words and their derivatives, including: metal dust, combustible, explosive, fire, zinc-aluminum alloys, shot blast, de-alloying, alloy separation, metal finishing, hazards, risks, and accidents.

Overview of Literature Search Results

The most relevant articles and information were acquired, and copies of the articles are included in the Appendix to this report. These articles contain a wealth of information about safety issues for fine dusts of many materials. For the purpose of this report, only key points are summarized, but the articles are attached for the reader who wishes to delve more deeply into the technical details of these matters.

The key takeaways from the literature search may be summarized as follows:

1. Nearly all finely divided metals or organic materials have the potential to combust (react with oxygen in the atmosphere) and thus pose a potential safety hazard.
2. Combustability and explosivity are related; explosions are special cases of rapid combustion in confined spaces where the combustion is so rapid that a detonation shock wave occurs, capable of causing physical damage to the surroundings.
3. Many process industries face and deal with the potential hazards of fine dusts, including metal fume collection from melting/welding operations, polishing/buffing operations, powder metallurgy operations, coal dust generation, and grain processing/storage.
4. Finely divided aluminum is particularly notable because of its very high heat of formation for the oxide (exothermic release of energy), and many articles have focused on explosions in process equipment handling fine aluminum dusts.
5. It is important to understand the factors affecting the potential hazards for fine dusts. It is not accurate to make a general statement that one material is more hazardous than another under all circumstances. Key factors that must be considered include:

   <u>Composition</u> – Metals vary in their reactivity with oxygen, and may be compared on the basis of the enthalpy of formation for their oxides. Table 1 below compares the reactivity of common metals in terms of the kcal/mole of energy released per mole of metal converted to oxide.

Table 1. Reactivity of common metals with oxygen.

Metal	Oxide	kcal/mole of metal in oxide
Al	Al_2O_3	-834.9
Cu	CuO	-155.2
Fe	FeO	-272.0
Fe	Fe_3O_4	-372.3
Fe	Fe_2O_3	-413.0
Mg	MgO	-601.0
Ti	TiO_2	-944.0
Zn	ZnO	-348.0
* Source - NIST Chemistry WebBook		

Thus, it may be seen that zinc dusts are similar to iron in term of reactivity potential with oxygen and significantly less reactive than elements such as aluminum, titanium, and magnesium. This information does not address reactivity of alloys such as Zn-4Al, although by percentages, the reactivity of the alloy would be expected to be very much closer to that of zinc than aluminum.

Particle size – the reactivity of a batch of material increases by the amount of surface area exposed for reaction with oxygen, and the surface area increases as the inverse square of the particle diameter.

Jacobson et al.'s Bureau of Mines work [1] is the classic work on explosibility of metal powders and includes tables with extensive information about threshold temperatures and spark energies for many metals and alloys of various sizes. Most of the data applies to particle sizes of 100-325 mesh (149-44 microns).

Unfortunately, zinc-aluminum alloys were not characterized, but it may be seen in Table 1 that alloying aluminum with almost any element dramatically reduces the powders index of explosibility. It may be seen further in Table 1 and Table A-1 that the sensitivity of zinc dusts to explosion or ignition is low.

Extremely fine particles (less than 1 micron diameter) for most materials give rise to special concerns about pyrophoricity and explosivity. However, the vast majority of dust collected in baghouse dust collectors from shop blasting operations is in the 100-325 mesh size range and considerably too coarse for these considerations.

Ignition source – Fires or explosions require a threshold temperature to be exceeded or an ignition spark (e.g. from a static electricity discharge). Jacobson et al.[1] also includes tables with extensive information about threshold temperatures and spark energies for many metals and alloys of various sizes.

Typically, modern shot blast cabinets are electrically grounded to prevent static electricity discharges and fires are quite uncommon, particularly when the equipment is cleaned and maintained properly.

Extent of surface oxidation – Metal dusts that are generated in an air atmosphere (e.g. grinding or shot blasting) develop an oxidized surface layer as processing proceeds, unlike processes that create relatively pure or nascent metal surfaces (vacuum melting condensates and some polishing operations). Dusts with surface oxidation are significantly less reactive than non-oxidized ones, but can still be ignited with higher applied energy.

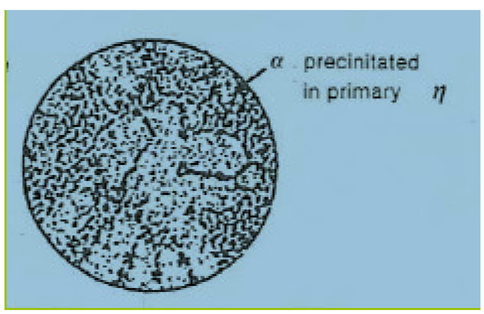
Concentration and Agglomeration – Dust explosions require a threshold concentration of particles in a cloud of dust confined in an enclosure[2-5]. Process conditions where dusts collect on surfaces or cake together are less hazardous than when dusts are billowing in turbulently at a critical threshold concentration. The presence of inert materials in a metal dust cloud can lower the potential for explosions, and such materials are commonly added intentionally in pure aluminum buffing processes for this reason[6].

Potential for De-alloying or Separation of Zinc and Aluminum Content

No citations were found in the literature search indicating a potential for de-alloying zinc-aluminum in metal finishing operations that might create a potential hazard from aluminum dust fires or explosions.

The concern here was that mechanical abrasion of the Zn-4Al shot during shot blasting might shatter the metal fines into zinc-rich and aluminum-rich particles, and the aluminum-rich particles might give rise to a greater fire or explosion hazard.

Casting zinc shot alloyed with 4% aluminum creates a final microstructure having a large fraction of a zinc-rich (eta) phase containing a fine dispersion of aluminum-rich (alpha phase) particles, as shown in the schematic below.



Both the matrix and the precipitates have moderate ductility, based on knowledge of this alloy's characteristics for commercial die castings. Separation of the alloy through mechanical action is not believed to be possible, much in the same way that pulverizing cannot separate brass into copper and zinc, bronze into copper and tin, or steel into iron and carbon (or other alloying additions). Any metal fines from the breakdown of ZA-4 shot are expected to remain alloyed, and their propensity to react with oxygen should be nearly identical to pure zinc fines of the same size.

Experiment to Investigate Potential for De-alloying/Separation

Transmet conducted an experiment at MTI's recommendation to investigate whether separation and concentration of aluminum-rich fines might be possible when shot blasting using Zn-4Al shot.

The experimental procedure was as follows:

A 100 g sample of Transmet's Zn-4Al shot was processed using an Ervin Industries Abrasive Test Machine, which is used for life testing of the shot. The apparatus was run for 2,000 cycles. Metal fines were collected and passed through a 60-mesh screen to collect particles less than 250 microns in size. Additional 100 g samples were processed in this same manner until a total of 300 g of fines less than 250 microns in size had been collected.

A 0.75 in.-diameter graduated cylinder was filled with the metal fines to the 40 ml mark of the cylinder. The graduated cylinder was secured to a QuantaChrome AUTOTAP (Ro-Tap) machine and tap-vibrated for 2,600 cycles.

The hypothesis/expectation here was that density variations would cause low density, aluminum-rich particles to rise to the top, and higher density, zinc-rich particles would segregate to the bottom.

The top 25% of the fines were carefully collected and labeled. The middle 50% of the fines were removed and discarded, and the bottom 25% were again collected and labeled.

A second batch of Zn-4Al shot was also processed using the same procedure as above, but this batch was artificially aged (185 F for 8 hours in a Lindberg Blue M Stabil-Therm electric furnace). The purpose of this test was to investigate whether the behavior of the shot might change over time.

The top 25% and bottom 25% samples for both the as-cast and artificially aged batches were sent to NSL Analytical for chemical analysis by inductively coupled plasma (ICP) spectroscopy, and the test results for aluminum content are shown in Table 2 below.

Table 2. Aluminum content for Zn-4Al shot fines to

	As-Cast		**Artificially Aged**	
	Top 25%	**Bottom 25%**	**Top 25%**	**Bottom 25%**
% Aluminum	**3.93**	**3.97**	**3.92**	**3.96**

The test results indicated that the aluminum content in the top portion and the bottom portions for both the as-cast shot and the artificially aged shot were nearly identical, indicating that no elemental segregation had occurred and that this result is independent of shelf life for the product. Metal fines generated by shot blasting remain alloyed.

Conclusions

- No citations were found in the technical literature search indicating that zinc-aluminum alloy fines generated by shot blasting are more hazardous than fines generated by other types of shot media.
- No evidence was found in the technical literature search indicating that zinc-aluminum alloy can separate into zinc-rich and aluminum rich phases by mechanical means such as shot blasting.
- An effort to segregate zinc-rich and aluminum-rich fines by density using a Ro-Tap apparatus failed did not result in any segregation by aluminum content.
- MTI concludes that fines generated by shot blasting using Zn-4Al remain alloyed, and these fines are no more hazardous than metal dusts generated by other conventional shot blast media.

References

1. “Explosibility of Metal Powders, M. Jacobson, A. Cooper, and J. Nagy, U.S. Bureau of Mines, Report of Investigations 6516, 1964.
2. “Understanding Dust Explosions” - The Role of Powder Science and Technology, R.K. Eckoff, KONA No. 15, 1997.
3. “Aluminium dust explosion risk analysis in metal workings,” L. Marmo, D. Cavallero, and M.L. Debernardi, Journal of Loss Prevention in the Process Industries 17 (2004), 449-465.
4. “Explosion temperatures and pressures of metals and other elemental dust clouds,” K.L. Cashdollar, and I.A. Zlochower, Journal of Loss Prevention in the Process Industries 20 (2007), 337-348.
5. “Overview of dust explosibility characteristics,” K.L. Cashdollar, Journal of Loss Prevention in the Process Industries 13 (2000) 183–199.
6. “Reducing aluminum dust explosion hazards: Case study of dust inerting in an aluminum buffing operation,” T.J. Myers, Journal of Hazardous Materials 159 (2008), 72-80.

Sincerely,

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