Fire and Materials Research Laboratory

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Improved Reaction-To-Fire Test for Particulate Metals and Method to Evaluate the Efficacy and Limitations of Liquid Suppressant Agents for Metals Fires and Waste Hazard Reduction

FINAL REPORT

BAA Project No. #78
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ABSTRACT

The UN Dangerous Goods Tests and Criteria Test N.1: Test Method for Flammable Solids applies to metal and non-metal substances. Metal and metal alloy fires are different from non-metal fires in that they typically burn at higher temperatures and are difficult to extinguish. Like non-metals, finely divided, high surface area metals can ignite readily, burn rapidly, and have a greater propensity for flash fire and/or explosion if dispersed in air. Research and testing with eleven (11) particulate metals, including mixtures and various physical forms, showed burning rates ranging from 0.01 to 38 mm/s—a majority (85%) burned at a rate less than 16 mm/s. Some metal samples were ignited with sparks; some metal samples did not ignite when a propane-oxygen torch flame was applied. Most samples burned with temperatures well in excess of 1,000°C and as high as 1,700°C. An improved test method and criterion for flammable solids that distinguishes between intermediate (Packing Group II, Category 1) and lower (Packing Group III, Category 2) hazardous substances offered for transportation is proposed. Specifically, a more robust screening test is proposed using a stronger ignition source and requires the finest fraction be isolated for testing before exclusion from Division 4.1. Further, for the full burn rate test, the burning rate criterion was increased from 5 minutes to burn 100 mm (0.3 mm/s) to 25 s (4 mm/s); the upper limit of burning duration (e.g., 10 minutes) was removed; and, a lower limit identifies highly hazardous metals and metal alloys. Text, a flow chart, and a table of metal and metal alloy examples are presented. The test procedure language includes the important limitation that the burning rate test does not identify flash fire or explosion hazards; a not Division 4.1 flammable solid can still be explosible. Instrumented intermediate-scale tests with material trains 1.2 m in length were performed to validate the bench scale tests and to examine the efficacy of three suppression agents for metal fires.

EXECUTIVE SUMMARY

The project's scope was to technically review the test method for flammable solids for metals and metal alloys, identify gaps and limitations in the test method, and recommend improvements that consider different forms and compositions including variations in moisture content, admixtures, and contaminants (e.g., cutting fluids). The general test procedure is widely used and easy to execute. Table 1 is the current test and criterion for metal powders. Table 2 is the proposed criterion for particulate metals including dust, powders, fines, chips, turnings, swarf, rock, and sponge. Figure 1 is a flow chart for assigning flammable solid, metal and metal alloys to Division 4.1.

Table 1 Packing group (PG) assignment after ignition by gas flame with minimum temperature 1000°C

Burning duration (min)	Burning rate (mm/s)	Packing Group
<5	>0.3	II
5 to 10	0.17<rate<0.3	III

Table 2 Proposed packing group (PG) assignment

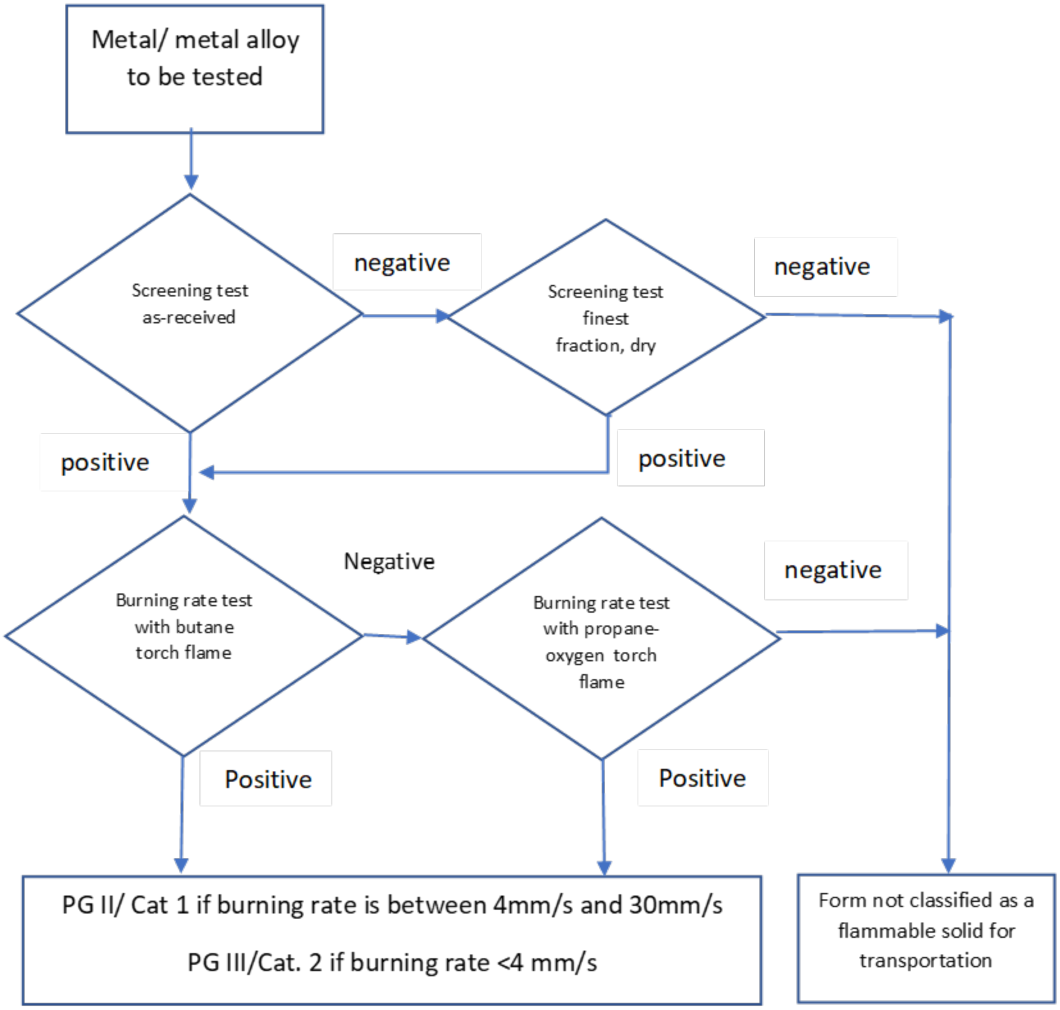
Time to propagate 100 mm (s)	Burning rate (mm/s)	Ignites by spark, butane, or propane-oxygen torch flame
3 to 25	4<rate<30	PG II
>25	<4	PG III

The proposed screening and burn rate tests use a stronger ignition source (propane-oxygen torch flame) to reduce the occurrence of false negatives possible with a weaker ignition source. The burn rate test includes an optional spark ignition source to identify readily ignitable metal and metal alloys; these would likewise ignite upon momentary application of a butane torch flame. An added screening test for negative, as-received metals after sieving and/or drying also would eliminate false negatives due to contaminants; the faster burning rate metal is classified. The burning duration of 20 minutes or less for the screening test should capture metal and metal alloys that propagate burning away from the ignition source.

There are currently three categories for metal and metal alloys that ignite and burn that are not pyrotechnic mixtures: PG II (Cat. 1) flammable solid, PG III (Cat. 2) flammable solid, and not Division 4.1 flammable solid. The Test N.1 criterion for distinguishing PG II from PG III is 5 minutes to burn, react, smolder, or spread 100 mm, or a burn rate 0.3 mm/s. This burning duration is too long, and the burn rate is too slow as it describes most metal and metal alloys that ignite and continue to burn. Further, the criterion does not distinguish between metal and metals alloys that ignite readily and burn vigorously from those requiring a higher ignition energy and/or burn slower. As a result of testing, the burning rate criterion was increased from 0.3 mm/s to 4mm/s or the burning duration decreased from 5 minutes to 25s to burn 100mm which is more consistent with the intent of the test to differentiate metals that burn rapidly from metals that propagate

combustion by slow burning or smoldering. Two metals burned faster than 30 mm/s; these outliers represent high hazard materials or metals in high hazard form or condition.

Figure 1 Proposed flow chart for the classification of flammable metal and metal alloys



Five recommendations are proposed:

1. Packing Group II/Category 1 is assigned to metal and metal alloys, in any form or concentration, that can be ignited by a spark, butane torch flame or propane-oxygen torch flame and propagate burning 100 mm in 25 s or less or a burning rate faster than 4 mm/s.
2. Packing Group III/Category 2 describes metal and metal alloys, in any form or concentration, that can be ignited by a butane torch flame or propane-oxygen torch flame and propagate burning 100 mm in longer than 25 s or burning rate slower than 4 mm/s.
3. Metals that burn 100 mm in less than 3s (>30 mm/s) should be classed as highly hazardous; a separate hazard class or PGI assignment should be considered.

4. The upper time limit for burning duration is removed; a metal or metal alloy that propagates burning the entire length, the 100 mm burning distance inclusive, should be included as a flammable solid.
5. ‘Form not classified as a flammable solid for transportation’ describes a metal that, in five trials, does not ignite when exposed to a propane-oxygen torch and does not propagate away from the location of the torch.

The proposed improvements will resolve false negatives and should better identify metal and metal alloys that burn rapidly from metals that are more difficult to ignite and spread burning slower. Proposed language modifying the existing Test N.1 method, in legislative format, a table of examples and flowchart are in Appendix 1.

INTRODUCTION

Physical tests are an important element of fire risk assessment. Where gaps in and limitations of existing test methods are identified, a new test can be developed, or the existing test method can be improved. One way to improve an existing test is to adjust the criterion for classification. Additional text and guidance can address variations in materials that may influence a fire hazard assessment that may be encountered. False negative results should not occur, and highly hazardous materials and/or conditions should be identified. Conditions that can result in false negatives are terminology, a single ignition source, and no guidance on how to address mixtures. Metal-containing mixtures include alloys, water, cutting fluids, and contaminated metal powder, such as from three-dimensional printing operations, that can have a major influence on ignition propensity and burning behavior. The Test N.1 test method is simple to execute and to record results. A major limitation of the method, however, is a lack of correlation with the same material when dispersed in air that can result in a flash fire or explosion. Some metal and metal alloys that are not Division 4.1 flammable solids may be explosible.

New products offered to replace or compete with existing products should be demonstrated to perform the same or better and not cause an increase in hazard[1]. Procedures can be developed to compare the performance of products. An instrumented intermediate-scale test with burning metals was developed to assess the performance of two liquid suppression agents. The response of application of a suppression agent from a pressurized, hand-held extinguisher was documented with video recordings, thermal imaging and temperature data from an embedded thermocouple.

A cross section of metal and metal alloys ranging in form and concentration were selected to represent materials in production, commerce, recycling, and waste. The samples tested ranged from custom alloy powders to machining swarf and metal-containing process dust from dust collectors. Some metal and metal alloys were purchased; others were received. Each metal and metal alloy were characterized and then subjected to instrumented bench and, in some cases, intermediate scale testing. The bench scale test examined three ignition sources, solutions for materials that did not conform to the mold used to create the prismatic train, and the influence of form, particle size, moisture content, and contaminants on ignition propensity and burning rate. The intermediate scale test was used to validate the bench scale test and to measure the effect of liquid suppression agents discharged onto burning metal.

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[1] ASTM E1776-16 Standard Guide for Development of Fire-Risk-Assessment Standards

UN TEST N.1 TEST FOR FLAMMABLE SOLIDS

The stated purpose[2] of the test for flammable solids, regardless of composition, is as follows:

> *to differentiate between substances that can be ignited and those which burn rapidly or whose burning behavior is particularly dangerous, only substances whose burning rate exceeds a certain limiting value are classified in the class of flammable solids' and 'the test procedure…adequately assess the relative hazard…*

The test method distinguishes between non-metals and metal or metal alloy powders. The ignition source is the same for metal and non-metal samples, but the criteria for classification are different. The burning duration to propagate 100 mm is 45 s for non-metal (2.2 mm/s) and 5 minutes (0.3 mm/s) for metal; there is no basis for the difference in burning rate criterion for non-metals compared to metals. The test method references one form of metal and metal alloys: powders. Yet, it is recognized that there are many other forms of metal and metal alloys that can ignite and burn.

The metal 'powder' is formed into a continuous train using a mold. A gas flame with minimum temperature 1,000°C is then applied to one end for up to 5 minutes. If ignition does not occur after a single test, the material is considered a 'not Division 4.1 flammable solid.' If ignition and propagation occur along the full length of the train in less than 20 minutes, the full burn rate procedure is performed. The full burn rate procedure involves six (6) trials where one end of a train of material in its commercial form is exposed to the same gas flame. If ignition occurs, then the time for the burning metal to travel 100 mm is recorded. The burn rate is calculated. If one or more tests result in propagation in less than 5 minutes, the metal is classed as PG II (Cat. 1) if the duration to spread 100 mm takes 5 to 10 minutes, the metal is assigned to PG III (Cat. 2). Metals that propagate slower than 0.17 mm/s, or100mm in longer than10 minutes, are excluded from classification.

Burning rates on the order of 0.3 mm/s are not consistent with 'burn rapidly' as the test intends. Some metal and metal alloys may require a stronger ignition source than non-metals. The test method provides no guidance for testing and classifying admixtures, moist or wet mixtures, contaminated metals, powders that do not conform to the mold (e.g., swarf, rock, sponge), or materials with a range in particle sizes.

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[2] UN Manual of Tests and Criteria Section 33 Classification Procedures, Test Methods and Criteria Relating to Flammable Solids, Solid Desensitized Explosives, Substances Liable to Spontaneous Combustion and Substances Which, in Contact with Water, Emit Flammable Gas.

MATERIALS

MATERIAL CHARACTERIZATION

Composition. If manufactured (e.g., metal powders), the product label, certificate of analysis, product data sheets, or safety data sheet contains the chemical composition. Otherwise, the chemical composition of metal, metal alloys, and mixtures was determined using Scanning Electron Microscopy (SEM) with elemental analysis using Energy Dispersive X-ray (EDS) spectroscopy. EDS is capable of reliably identifying chemical elements to at least 1 weight percent. Additional interpretation is required if the EDS spectra shows carbon and/or oxygen, which may be attributed to oxides, carbonates, and/or other contaminants (oils, cutting fluids, etc.). Moisture, if present, was measured gravimetrically using a moisture analyzer or by weighing a tray of material before and after drying in a laboratory oven.

For this project, a JEOL JSM-IT500 SEM/EDS at 20 keV was used to determine chemical composition. An AND MX-50 moisture analyzer was used to measure moisture content. A Yamoto Model DVS402 drying oven was used to dry metal samples at 100°C to 105°C, when required.

Shape. Particulate metal and metal alloys range in source and shape. Terms used to describe the shape of particulate metal are sponge, rock, turnings, ribbon, swarf, chip, shavings, fines, powder, nano-powders, and dust. Turnings and ribbons are further described as coarse, medium, or fine. Fines and powders are further defined as spherical, angular, acicular, irregular, etc. Fines described by one manufacturer referenced the source: saw fines, grinder fines, saw swarf, and sponge (-20 mesh). Macro photographs, microscopy using either a Keyence VHX digital microscope or Nikon stereomicroscope, and SEM were used to document each metal sample's form and particle morphology.

Particle Size. Surface area strongly correlates with reactivity including combustion. Surface area generally increases from sponge, rock, turnings, ribbon, swarf, chip, shavings, and fines to powder and dust. Particulate metal, metal powders, and mixtures may have a wide or narrow range in particle size. Dust and processed metal powders have a narrow particle size range compared to fines, turnings, rock, and sponge. Data from simple sieving to determine the weight fraction of particles within a size range are useful in assessing hazard potential: more finer particles are typically higher hazard. Image analysis software allows for particle size measurements by tabulating the range, diameter, or maximum and minimum dimensions. Dust particles may be analyzed at high magnifications, at least 1000 times magnification, using an SEM.

In this project, the particle size was ordered and/or reported by the supplier or determined using a Gilson sieve shaker (Silent Sifter II SS-22) with 10 calibrated sieves ranging from plus 6 mesh (>3.3mm) to minus 325 mesh (<45 micron). For the screening test, fines with particle sizes less than at least 500 microns are proposed before exclusion from Division 4.1. Some saw fines or swarf and turnings cannot be sieved but their width dimension can be measured.

All metals and metal alloys were stored in their original containers inside a flammables cabinet at room temperature.

IGNITION SOURCES

The current UN Test N.1 specifies one ignition source: ‘a hot flame (minimum temperature 1000°C) from a gas burner (minimum diameter 5 mm)’. In this project, three, readily available ignition sources were characterized and used.

Flint-Style Spark. A readily available ferrocerium campfire flint-style spark device was used. From EDS, the rod composition was 44 wt% cerium, 38% lanthanum, and 8% iron. When scraped with the edge of the steel scraper provided with the tool, the rod throws white sparks up to 0.3m (12 in.) from the tool. One ferrocerium fire starter supplier reports “molten spark showers at 3,000°C (5,500ºF)”.

Butane Gas Torch. Two re-fillable butane gas torches[3] (Bernzomatic) from hardware stores were characterized by mass loss (fuel consumption), flame temperature, flame shape, and flame length. Each torch was set on the HIGH setting and filled with butane prior to igniting. The blue flame temperature ranged from 1,050°C to 1,150°C. The mass loss rates were 0.26 to 0.28 grams per minute. Using the heat of combustion of butane gas (-2,878 kJ/mol), butane molecular weight (59 g/mol), and the measured mass loss rate (0.004 g/s), the butane torch flame is approximately 200 Watts. One torch had a needle-like flame that was approximately 70 mm (2.75 inches) in length. The second torch flame was horizontal from the nozzle then bent upward and 51 mm (2 in) in length. Both torches were capable of igniting titanium powder (-100+325mesh or less than 150 microns but greater than 44 microns) in less than 5 minutes. The Bernzomatic 3-in1 Micro torch/soldering iron (Model ST2200, www.worthingtoncylinders.com) with the blue, needle-like flame on the HIGH setting in the continuous mode was used in the bench-scale testing.

Propane-Oxygen Torch Flame[4]. A propane-oxygen torch flame represents higher than typical piloted ignition sources. Torch kits with propane and oxygen gas bottles, hose, and torch head are readily available. The volume of oxygen to a propane flame is increased until a noisy, blue, torch flame results. Propane-oxygen torch flame temperatures average 1,650°C.

DATA ACQUISITION

Individual tests were recorded using photographs (Olympus), video recordings (Sony, GoPro), and thermal imaging (FLIR T660). The FLIR T660 thermal imaging video camera has a temperature range up to 2,000°C. Direct temperature measurements were made using either fiberglass-insulated K-type thermocouples or ceramic insulated S-type thermocouples and recorded using a

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[3] https://www.bernzomatic.com/Products/Hand-Torches/Manual-Ignition/WK5500OX

[4] While acetylene gas torch flames likely have high temperatures similar to propane-oxygen torch flames, the goal is to specify a torch for consistency in results. Propane-oxygen torches are adequately sized and available for lab use.

four-channel DAQ with software by Madgetech. Each DAQ thermocouple connector was periodically checked with a Fluke thermocouple calibrator. Temperature data were recorded at 1 s intervals.

CERAMIC TEST PLATES

Flat plates and plates with triangular cross section wells or troughs were cast using Mizzou castable high alumina material for use up to 1,648°C (3,000°F). The dimensions of each plate were 24 cm x 24 cm x 2.5 cm thick. A rubber mold was made using the outside dimensions of the flat plate and the plate with a V-shaped trough. The dimensions of the trough created along the diagonal of a 24 cm^2 plate were 33.5 cm long by 2.25 cm wide by 1.1 cm deep. The castable ceramic was prepared according to the manufacturer's instructions and poured into the rubber molds. The plates set within 24 hours after pouring and were cured in a laboratory oven at 80°C (176°F) for 12 to 24 hours. SEM EDS analysis of plate composition after curing was 34 wt% aluminum, 13 wt% silicon, 5 wt% calcium, and 46 wt% oxygen. The plates did not exhibit heat stress, cracking, or deterioration during or after repeated exposure to burning metal.

SUPPRESSION AGENTS

A Class D fire extinguisher was purchased from Grainger. F500 Encapsulator was purchased from Hazard Control Technologies (hct-world.com, Hazard Control Technologies, Inc., 150 Walter Way, Fayetteville, GA 30214). Firebane was provided by Spectrum FX (spectrumfx.net, Spectrum FX, 9733 E. 54th Street, Tulsa, OK 74146). A rechargeable, hand-held fire extinguisher pressurized to 100 psi with air was used to discharge the two liquid extinguishing agents onto burning metals.

SUMMARY OF TEST METHODS

BENCH-SCALE TESTING

After characterization, the metal or metal alloy sample was formed into a continuous train on a ceramic test plate in a laboratory hood. In most tests, two S-type thermocouples were positioned at 80 and 180 mm from one end of the 250 mm train. A butane torch flame was applied to one end for up to 3 minutes (180 s). If ignition occurred, the time for the burning front to travel 100 mm and temperature were recorded. If ignition did not occur or occurred but did not propagate, a propane-oxygen torch flame was applied to the opposite end of the train for up to 1 minute (60 s). If ignition did not occur after exposure to a propane-oxygen torch flame, the metal was considered not flammable. If ignition occurred, burning rate and temperature were recorded. Burning duration was determined using a stopwatch and confirmed with review of video recordings and compared with the response of thermocouples as the burning metal propagated past the embedded thermocouples. Both the time between the initial increase in temperature and the peak temperature at each thermocouple were analyzed. The burning behavior was noted. Observations included burning as bright condensed phase combustion with no flames; bright burning with flames; flame height; prolonged glowing after the burning front passed; irregular burning front; burning ejecta (e.g., sparklers) from the metal, etc.

Where required, the following modifications were made:

- Swarf, turnings, rock and sponge that did not conform to the mold were formed into a continuous train on the ceramic test plate and packed as tightly as possible.
- Samples from machining operations (e.g., swarf, turnings) were tested before and after washing and drying to remove water, cutting fluids or other contaminant.
- Spherical powders that did not conform to the prismatic mold (e.g., spread from pile when the inverted mold was removed) were poured and leveled into a ceramic test plate with a trough having the same dimensions as the prismatic train.

INTERMEDIATE-SCALE TESTING

Instrumented intermediate-scale tests with metal and metal alloys were performed in the burn facility under a large hood with the exhaust collection system set to low (e.g., 50% capacity). Two commercially available suppression agents (F-500, Firebane) were used at concentrations recommended by the manufacturer. The F-500 was diluted to 3% and 6% by volume with water; the Firebane was used as-received. A rechargeable, portable fire extinguisher was filled with the suppressing agent then charged to 100 psi with compressed air. The canister was weighed empty, after charging with extinguishing agent, and after discharging the liquid agent onto the burning material. The discharge from the nozzle was characterized as a spray pattern that projected approximately 2.7 m (9 ft) from the nozzle.

For the prismatic train tests, a wood-framed, cement-board (1.27 cm/ 0.5 in Dura-rock) lined enclosure was constructed with the following dimensions: 0.43 m (17 in) high, 0.76 m (30 in) deep, and 1.52 m (60 in) long. Particulate material was transferred to a mold formed by two 90-degree angle aluminum stocks with an overall length greater than 1.2 m (48 in). After filling the mold, the walls were removed, resulting in a prismatic train approximately 3.5 cm (1.3 in) height and 10 cm (3.9 in) wide at the base. Four ceramic insulated S-type thermocouples (TCs) were embedded in the material. From one end of the train, the TCs were positioned at 0.25 m (10 in), 0.51 m (20 in), 0.76 m (30 in), and 1.0 m (40 in). Temperature data were recorded using a MadgeTech four channel data acquisition system at 1 second intervals. The ambient temperature in the burn room was recorded before each test. The tests were documented with photographs, video recordings, and a thermal imaging video camera.

TEST RESULTS

BENCH-SCALE TESTS

The metal, metal alloys, or metal-containing mixtures were procured (e.g., commercial products), sampled from production, or production by-products including dust from dust collectors. None of the metal-containing mixtures were pyrotechnic- or exploding target mixtures. Table 3 summarizes the bench-scale burning rates of the metals, metal alloys, and metal-containing mixtures evaluated. Metals that did not ignite were exposed to a butane torch flame for 180 s at one end of a prismatic train of material and a propane-oxygen torch flame for 60 s at the other end. Table 4 compares the ignition source sensitivities of the metals that did ignite and burn.

Table 3 shows burning rates ranged from 0.01 to 38 mm/s. The fastest burning rates were 38 mm/s from dry, high surface area titanium powder followed by 33 mm/s from zirconium powder with 5 to 6 weight percent moisture. Eight (8) metal, metal alloys, or metal-containing mixtures did not ignite when exposed to the butane and propane-oxygen torch flames. Six (6) metal alloys or metal-containing mixtures ignited and smoldered or burned the entire length of the material train. The behavior ranged from slow smoldering (0.01 mm/s) with a wisp of smoke to very rapid burning over 30 mm/s with flames extending greater than 30 cm above the metal sample train.

Form, metal, composition, particle size and moisture content, in that general order, influenced ignition propensity and degree of burning.

Table 3 Summary of bench scale test data

<table>
<tr><th colspan="2">IGNITES AND BURNS</th></tr>
<tr><th>Metal/Alloy/Metal-Containing Mixture</th><th>Burning Rate (mm/s)</th></tr>
<tr><td>Titanium (Ti)</td><td>0.8 to 38</td></tr>
<tr><td>Titanium alloys</td><td>0.7 to 7.1</td></tr>
<tr><td>Zirconium (Zr)</td><td>5 to 33</td></tr>
<tr><td>Steel process dust</td><td>0.40</td></tr>
<tr><td>Magnesium (Mg)</td><td>0.20</td></tr>
<tr><td>Zinc process dust</td><td>0.01</td></tr>
<tr><th colspan="2">DID NOT IGNITE (DNI)</th></tr>
<tr><td colspan="2">Aluminum powder (Al)
Nickel (Ni)
Iron (Fe)
Aluminum process dust
Silicon (Si)
Zinc (Zn)
Tantalum alloy (Ta-W)
Manganese (Mn)</td></tr>
</table>

Table 4 Particulate metal and metal alloy ignition propensity

Metal, metal alloy, or mixture	Form	Spark	Butane Torch Flame	Propane-Oxygen Torch Flame
Magnesium	Chip		X	
Steel process dust	Dust		X	
Titanium	Dust	X	(X)	
	Powders		X	X
	Chip, fines			X
	Swarf (dry)	X	(X)	
	Sponge			X
Zinc process dust	Dust		X	
Zirconium	Fines	X	(X)	
	Rock, small		X	

Note. (X) means if a spark ignites the pile, a butane torch flame will ignite the pile

The following eight metals, metal-alloys or metal-containing mixtures did not ignite: aluminum powder, nickel, silicon, iron, manganese, zinc, and a tantalum-tungsten alloy (Table 3). These same metals are each known to ignite under the conditions of being dispersed in air in the presence of an ignition source, resulting in a flash fire and/or explosion. For example, aluminum powder formed into a pile does not ignite and burn when exposed to torch flames, but aluminum dust was responsible for 28 fires or explosion incidents causing 62 injuries and 15 fatalities from 1998 to 2005.[5] Reported ignition sources for these incidents included explosion, flame, metal strike, spark, static, and unknown.

Detailed descriptions, representative photographs, and temperature profiles for each metal and metal-alloy tested at the bench scale are included in Appendix 2.

INTERMEDIATE-SCALE TESTS

Four forms of particulate titanium (dust, sponge, fines and saw fines) were subjected to a series of intermediate scale tests with two liquid and one Class D suppression agents. The goals of the intermediate scale test were to 1) validate the bench scale (250 mm train) test; 2) evaluate various suppression agents; and 3) compare and evaluate two liquid suppression agents used for small metal fires. In one test, the burning metal was extinguished with a Class D fire extinguisher. The four titanium forms were sourced from three locations and had particle sizes ranging from dust (floor sweep) to saw swarf[6]. The action of and reaction between the suppression agent and burning metal was monitored visually, using thermocouples, a thermal imaging camera, and video recordings.

Table 5 summarizes tests performed with a 1.2m length prismatic train for each titanium sample. One trial was performed with the same titanium floor sweep/dust but in a shallow steel drum. Unlike the flat surface on which the prismatic trains were prepared, the shallow drum contained the liquid suppressant agent.

Table 5 Summary of intermediate-scale tests performed

Form of Titanium	No. Trials	F-500	Firebane	Class D
Dust (floor sweep)	2	x	x	-
-40 Mesh Sponge	3	x	x	x
Fines	1	x	-	-
Saw fines (as received)	1	-	x	-

The burning behaviors of the various titanium forms is summarized in Table 6. All particulate metals were ignited using a MAPP gas torch. Once ignited, burning was sustained, and propagated

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[5] https://www.csb.gov/combustible-dust-hazard-investigation/Dust Incident Data Fie

[6] The dust sample was referred to as ‘floor sweep’. The saw fines were from a drum labeled ‘Titanium fines, saw fines, saw swarf, and sponge’.

the entire length of the train of material. Burning rates ranged from 0.03 m/min or 0.5 mm/s for the dust followed by saw fines (as-received), which was 0.08 m/min or 1.3 mm/s. The minus 40 mesh sponge burned fastest at 0.6 m/min or 10 mm/s. The saw fines had an intermediate burning rate 0.24 m/min or 4 mm/s between fines and sponge. All the titanium burned bright with an orange flame and glowed after the burning front passed. The FLIR recorded the highest temperatures at the burning front, while the TCs recorded peak temperatures after the burning front passed. Peak core temperatures exceeded 1,600°C—temperatures capable of dissociating water into hydrogen and oxygen.

Table 6 Burning behavior of different forms of titanium

Form of Titanium	Burn Rate (m/min) [mm/s]	Avg. Peak Core Temperature (°C)	Avg. Delay to Peak Temperature (s)
Dust (floor sweep)	0.03 [0.5]	1,648	168
Saw fines (as received)	0.08[1.3]	1,588	83
Fines	0.24 [4.0]	1,634	121
-40 Mesh Sponge	0.60 [10]	1,641	112

The reactions between the three suppression agents and the burning metals are summarized in Table 7. Class D fire extinguishers, which consist of a dry powder discharged from a wide nozzle, smothered flames and covered the burning metal, decreasing the surface temperature and preventing the fire from propagating or advancing. Temperatures, however, remained high inside the pile. The responses of the liquid extinguishing agents to the burning metal resulted in a momentary decrease in temperature (e.g., cooling effect) with short term suppression of burning. The Firebane resulted in increased flames upon application. The F-500 suppression agent was effective on fines.

Table 7 Reaction between burning metal and suppression agent

Form of Titanium	F-500	Firebane
Dust	Jetting particles	-
Saw fines (as received)	-	Momentary fireball
Fines	Suppressed spread	-
-40 Mesh Sponge	-	Momentary fireball

Detailed descriptions, representative photographs, and temperature profiles of the intermediate scale test with the various forms of titanium and suppression agents are in Appendix 3.

ANALYSIS OF TEST DATA

PROPOSED IMPROVEMENTS TO UN TEST N.1

The results of the bench-scale testing were compared with the existing criterion for flammable solids as applied to metals and metal alloys. The metal and metal alloys tested exhibited a range in burning behavior, ignition propensity and burning rate. Table 8 summarizes the various metal and metal alloys tested in order of increasing burning rate. The dashed line divides, using the current burning rate criterion of 0.3mm/s, metals assigned to PG II (below the dashed line) and PG III (above the dashed line). As shown, the existing criterion applies to nearly all the metals that ignited and burned and does little to distinguish those that burn rapidlgy and those do not burn rapidly.

Not all particulate metals in a layer or pile, including dust and powders, are flammable solids. These metals resisted ignition from a propane-oxygen torch flame. Other metals, particularly metal powders and fines, required a propane-oxygen torch to ignite but once ignited continued to burn. Other metals ignited readily and burned rapidly as-received, over a narrow moisture content range, and after washing and drying. In other words, burning behavior and therefore burning rate can be conditional. Wet titanium swarf could not be ignited with a propane-oxygen torch flame but burned 16.6 mm/s when dried. The data also shows the same metal in different forms can exhibit the range in burning behavior.

Because the existing criterion is not meaningful given the range in burning rate, a new burning rate criterion was sought. From testing, metal and metal alloys regardless of form that burned 100 mm in 25 seconds or less or 4mm/s and faster were considered to meet the intent of test method to identify solids that 'burn rapidly'. Metal and metal alloys that ignited and burned slower than 4mm/s were not considered to burn rapidly. The burning rate data also shows what are considered highly flammable metals outliers that propagated burning over 100mm in 3 or fewer seconds. The highly flammable metals were low moisture content zirconium fines and powder and dry, high surface area titanium powder. The current test method for flammable solids does not include a PG I category.

Table 8 Burning rate (if at all) of various metal and metal alloys forms

Metal or metal alloy (concentration, form or size)	Proposed PG II/ Cat. 1 (faster than 4 mm/s)	Proposed PGIII/Cat. 2 (slower than 4 mm/s)	Not a flammable solid for transportation	Current Assignment
Ti sponge (-40 mesh)			X	Not regul.
Ti swarf (wet)			X	
Zr powder (wet)			X	4.1, II
Zr (sponge, rock, large)			X	4.1, III
Aluminum powder			X	4.3, II 4.1, II
Silicon (99%, -325 mesh)			X	4.1, III
Manganese (99%) (-100+140 mesh)			X	4.3, I 4.1, III
Manganese process dust			X	
Iron powder			X	
Nickel powder			X	
Tantalum-Tungsten alloy (-70+270mesh)			X	
Zinc process dust		0.01		
Magnesium chip (99%, 4-30 mesh)		0.26		III
Steel process dust		0.40		
CP Ti spherical powder		0.40		4.1, II
Ti6Al4V powder		0.70		4.1, II
CP Ti powder (angular, -100+325)		0.87		4.1, II
Zr (rock, small)		1.2		4.1, II
Ti chip		1.4-1.8		4.1, II
Ti (-270+500)		1.6		4.1, II
Ti (-60 mesh, HDH)		3.2		
Ti (97%)	4.2			4.1, II
Ti (saw fines, clean, dry)	4.3			
Zr (milled fines, 2% MC)	4.8			4.1, II
Zr powder (dry)	5.3			4.1, II
Ti powder (dry, -325 mesh)	5.6			4.2, II
Ti (-40mesh, sponge)	5.8			
Ti -5Al (dust)	7.1			
Ti swarf (33% MC)	8.3			
Ti swarf (24%MC)	11.1			
Zr powder (8.6%MC)	14.2			4.1, II
Ti swarf (dry)	16.6			
Zr powder (6% MC)	33.3			4.1, II
Ti (-100 mesh, Armstrong)	38.1			
MC= moisture content; HDH= hydride-dehydride, CP=chemically pure				

The test method and Packing Group criterion text should be revised to remove the word 'powder' in light of the various metal and metal alloys forms are manufactured, used, handled, captured, and stored. Other terminology may include "Metal and metal alloys, regardless of form" or "Metal and metal alloys, in all forms" or "metal and metal alloy powders, dusts, fines, chip, turnings, swarf, and sponge".

Screening tests are recognized as 'a fire-response test performed to determine whether a material, product or assembly (a) exhibits unusual fire-related characteristics, (b) has certain expected fire-related characteristics, or (c) is capable of being preliminary categorized according to the fire characteristic in question'.[7] The screening test for metal should utilize a stronger (worse-case) ignition source applied to the metal and metal alloy including mixtures. If the form, commercial or not commercial, of the metal does not ignite from a propane oxygen torch flame, it should be determined if the metal can be isolated from the mixture (by drying if wet or by washing and drying if contaminated with a cutting fluid or cutting oil). Similarly, if the form, commercial or not commercial, consists of a wide range of particle sizes, the finer fraction should be isolated and subjected to a strong ignition source. If both the commercial form and the finest fraction resist ignition and do not propagate burning after the ignition source is removed, the material is not in a form that is flammable for the purpose of transportation.

Ignition propensity and ease of ignition can be determined from the response of a material to ignition sources that range in energy and duration. The prescribed 'ignition source with minimum temperature 1000°C' can and has been shown to result in false negatives. In this case, a butane torch failed but a propane-oxygen torch ignited each of the following : titanium powder (CP, spherical); Ti6Al4V powder (-270 mesh); Ti6Al4Zr powder (-325 mesh); Ti3Al5V fines (-500 micron, -500+300 micron, and -300+150 micron), titanium chip, and titanium sponge. From these possible false negatives, once ignited the range in burning rate was 0.4 mm/s to 5.7 mm/s. Sparks from the ferrocerium rod were capable of igniting high surface area titanium (-100 mesh, HDH -60 mesh), dry titanium swarf, -325 mesh angular titanium particles, and zirconium fines. The metals ignited by spark had burning rates ranging from 4.2 to 38.1 mm/s. The inclusion of a high temperature ignition source, such as a propane-oxygen torch flame, will reduce the likelihood of false negatives.

Table 9 is a compilation of GHS and transportation assignments for various metals powders[8] assembled from a review of at least two supplier's safety data sheets. The results show some assignments inconsistent with current testing (e.g., silicon, manganese and iron as flammable solids); and some metals have different assignments (see manganese and titanium). Magnesium chip, which in this project had burning rate consistent with PG III, is not listed in the hazardous materials table.

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[7] ASTM E176 Fire Test Terminology

[8] The term 'powder' was used to in this search to ensure finely divided metals.

Table 9 Review of metal powder SDS classifications

Metal (conc.)	CAS	Size	HSC	UN	Division	PG	Source (SDS)
Silicon powder (>99%)	7440-21-3	-325 mesh, -60 mesh	H228	1346	4.1	III	Sigma-Aldrich, Gelest
Manganese (99%)	7439-96-5	-325 mesh	H260	3209	4.3	II	Sigma Aldrich
				3089	4.1	III	ESPI Metals
Aluminum	7429-90-5	75 um	H250		4.3	II	Sigma Aldrich
			H220	1309	4.1	II	Hummel Croton
Titanium (dry)	7440-32-6	45 um	H250	2546	4.2	II	Sigma Aldrich
Titanium and Ti-alloy powders		various		3089	4.1	II	ATI
Titanium sponge (>99%)	7440-32-6	Chunks, powder	None	NR	NR	NR	ATI
Zinc (>99%)	7440-66-6	<150 um	H410	1436	4.3/4.2	II	Sigma Aldrich
(92-98%)		Powder, dust		1436	4.3/42	II	Numinor
Zirconium		Powder, wetted	H251	1358	4.1	II	Hummel Croton
		Powder		1358	4.1	II	American Elements
		-100 mesh	H250	1358	4.1	II	Sigma Aldrich
Zirconium (60 to >99%Zr)		Chunks	Flam sol	3089	4.1	III	ATI

CAS= CAS number; HSC=hazard statements code; SDS=safety data sheet

There is an assumption that the bench scale test reflects the response of a metal or metal alloy or mixture on a larger scale. Intermediate-scale tests using the same metal tested at the bench scale but in prismatic trains with 1.2 m length were performed to validate the response of metals at a smaller scale. Once ignition and propagation of burning was established, three different extinguishing and/or suppression agents were applied and the response of the burning metal recorded.

PROPOSED TEST METHOD FOR METAL FIRE LIQUID SUPPRESSION AGENTS

Fires involving typical combustible fuels (e.g., non-metals) are chemically and thermally different than burning metal. The peak heat release rate is the defining property of non-metal fires, as the equations used to calculate the heat release rate are based on the combustion of typical hydrocarbon fuels. This is clearly not applicable to metal fires. Extinguishing media are oriented toward typical combustible fuel-fed fires with predictable peak temperatures. Not so with metal fires where elevated temperatures while burning results in suppression challenges. Class D powder fire extinguishers are approved for use on metal fires. Dry salt (sodium chloride) and dry sand are also used to smother metal fires. NFPA 484 *Standard for Combustible Metals* has a table in the annex with combustible metal fire extinguishing agents.[9] Water should never be applied to burning metal except, according to the table in NFPA 484, iron and steel.

There are liquid phase suppression or encapsulating agents proposed for use in suppressing metal fires by decreasing the temperature or slowing the spread of burning metal. Two liquid phase fire suppression agents were applied to burning metal on an intermediate-scale using a handheld fire extinguisher. NFPA 10 *Standard for Portable Fire Extinguishers* and NFPA 484 do not have guidance for testing the efficacy of new liquid-phase suppression and/or extinguishing agents on metal fires. NFPA recognizes UL 711 as the *Standard for Rating and Fire Testing of Fire Extinguishers*[10] which consist of various planned fires in a laboratory setting. From UL 711, 'these requirements also cover performance during fire tests of fire extinguishing agents for application on Class D fires' and Class D fires are defined as 'fires that involve combustible metals, such as magnesium, titanium, zirconium, sodium, lithium, and potassium'. The UL test for Class D extinguishers includes a magnesium chip fire with 18kg metal spread over 0.4 m^2 area that is accessible from all sides. A torch is used to ignite the bed of particulate metal. Extinguishment commences when burning is established (25% to 50% burned). The presence of unburned metal after the test is considered evidence of extinguishment.

> *Class D fire extinguishers, or an extinguishing agent arranged for manual handling, shall be capable of extinguishing combustible-metal test fires as designated for a given metal in the following, and of preventing the scattering of burning material beyond the test bed area during the conduct of the test. An extinguished test fire shall be in that state which is not subject to reignition under the conditions of test and shall contain enough unburned combustible metal to show extinguishment by the agent prior to burnout.*

The intermediate-scale tests were set up to establish burning of metal before the application of the suppression agent, to direct the suppression agent at the location of a thermocouple in the burning metal, to monitor with a thermal imaging camera and for adverse reaction. The test set up was repeatable allowing for different agents to be compared.

The different form of metals tested at the intermediate scale, once ignited, continued to burn. The burning rates at the bench scale and intermediate scale were compared. The minus 40 mesh titanium sponge particles' maximum burning rate 6.3mm/s at the bench scale and 10 mm/s at the intermediate scale. The titanium fines burning rate was 4.2 mm/s at the bench scale and 4.0 mm/s at the intermediate scale. Their general burning behaviors at the bench and intermediate scale were similar: the dust propagated slowly and retained heat or glowed longer; the saw fines burned with an orange flame and bright burning through the mass of metal.

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[9] NFPA 484 (2019) Standard for Combustible Metals, Table A.8.3.3.

[10] UL Standard 711 Rating and Fire Testing of Fire Extinguishers

The Class D fire extinguisher powder, like other inorganic solids including salt and sand, covered and stopped the burning metal. The liquid agents appeared to partially quench the burning metal with a decrease in temperature upon application but the metal was able to rebound and continue to burn. Thermal imaging was effective in comparing and monitoring the difference in temperature of the burned metal next to the location where the suppression agent was applied. Aside from the increase in flame height upon application, Firebane appeared to be effective in stopping the spread of the saw fines fire. An application of F500 slowed but did not stop the spread of the metal fire. More gaseous products and/or steam were evolved when the F500 suppression agent and burning metal were confined to a drum. Gaseous products and/or steam would have to be relieved from process equipment. The instrumented test method, overall, was effective in comparing the response of different suppression agents on metal fires.

DISCUSSION

Metal and metal alloys in particulate form have multiple, potential physical hazards which range from thermite reactions, pyrophoric reactions with air, fires, flash fires, dust explosions, and the evolution of flammable gases. Finely divided metal and metal alloys have a loss history: fatal flash fires at Hoeganaes involved the ignition of iron dust[11]; a fatal explosion at AL Solutions involved damp zirconium fines from a milling operation in a blender[12]; a large fire and explosion at a Los Angeles recycling facility involved reclaimed titanium in various forms[13]; and the Hayes Lemmerz explosion involved suspended aluminum dust[14]. Magnesium metal destroyed an Eaton Steel plant in central Michigan in May 2018; the form of the material first ignited is not clear but may have been particulate (e.g., dust) from processing[15].

Well-characterized particulate metal and metal alloys includes spherical metal powders made for additive manufacturing and powder metallurgy starting material with known composition, material specification, particle size, and range. Alternately, process dust and metal-containing waste are not as well characterized and may consist of a range in concentration. Admixtures require additional evaluation to determine if the finest fraction or a dry state behaves different from the as-received admixture, when sopping wet or coated with cutting fluid.

Combustible particulate metal and metal powder fires and explosions have occurred as a result of ignition by a cross section of ignition sources: electrostatic discharge, mechanical sparks including dropped tools, friction, hot surfaces, open flame, and exposure to other burning metals. Other ignition scenarios include elevated temperatures from thermite reactions and smoldering nests spreading to other combustible materials. Ignition of particulate metal and metal powders have

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[11] https://www.csb.gov/hoeganaes-corporation-fatal-flash-fires/
[12] https://www.csb.gov/al-solutions-fatal-dust-explosion/
[13] https://abc7.com/archive/7554195/
[14] www.csb.gov/hayes-lemmerz-dust-explosions-and-fire/
[15] www.wilx.com/content/news/Massive-fire-burning-at-manufacturing-plant-in-Eaton-Rapids--481462111.html

been established in solid layers from a hot surface[16] and when dispersed inside a chamber and exposed to pyrotechnic igniters[17].

The UN Test N.1 is used to identify particulate solids, metal and non-metal, that are flammable and to assign a packing group for transportation. The horizontal train test has a long history of use in determining the fire performance, both ignition propensity and burning rate, of various materials including mixtures. It was once used by the United States Bureau of Mines and GE Research to assess the burning rate of solid oxidizers mixed with sawdust.[18] Their proposed burning rate criterion to differentiate oxidizer-saw dust mixtures that had intermediate burn rate was 10-inches per minute, or 4.2 mm/s. Therefore, there is a historical basis for a 4 mm/s burning rate criterion.

The basic structure of the UN Test N.1 is currently used, although with differing criterion, by other regulatory agencies to assess and classify the fire performance of various materials, including waste (EPA Test 1030 *Ignitability of Solids*). The NFPA uses the basic test procedure to determine if a powder or dust (NFPA 652 *Standard on the Fundamentals of Combustible Dust*) or other form of metal (NFPA 484 *Standard for Combustible Metals*) is combustible and therefore subject to or excluded from the Code's requirements. Improvement in the existing test method for particulate metal and metal alloys could harmonize other regulatory fire hazard tests.

This fire risk assessment identified and addressed gaps and limitations of the UN Test N.1 test for flammable solids as applied to metals and metal alloys including waste. The intent of the test is to identify metal and metal alloys that can ignite; therefore, metal and metal alloy samples were exposed to ignition sources that ranged in energy and duration. A propane-oxygen torch was found to eliminate false negative test results. Materials that do not conform to the prismatic train can be tested if formed into a continuous train or trough. In general, the trough had slower burning rates than the material on a plate; the trough did not prevent propagation. The test criterion was revised to distinguish metal and metal alloys that burn rapidly, on the order of 4 mm/s or faster instead of the current 0.30 mm/s. Metals that propagate burning over 100mm in 3 seconds or less represent high hazard materials.

Additional research is required to classify the metals that have particularly dangerous burning behavior.

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[16] ASTM E2021 Standard Test Method for Hot Surface Ignition Temperature

[17] ASTM E1515 Standard Test Method for Minimum Explosible Concentration of Combustible Dusts

[18] Buc, E.C., NFPA Fire Protection Research Foundation Report, Enhanced Classification System for Oxidizers, 2006.

APPENDIX 1. PROPOSED REVISIONS TO DOT/ UN MANUAL OF TESTS & CRITERIA

DOT MANUAL

§ 173.124 CLASS 4, DIVISIONS 4.1, 4.2 AND 4.3 - DEFINITIONS.

(a) ***Division 4.1 (Flammable Solid).*** For the purposes of this subchapter, *flammable solid* (Division 4.1) means any of the following four types of materials:

(3) Readily combustible solids are materials that -

(i) Are solids which may cause a fire through friction, such as matches;

(ii) Show a burning rate faster than 2.2 mm (0.087 inches) per second when tested in accordance with the UN Manual of Tests and Criteria (IBR, see § 171.7 of this subchapter); or

(iii) Any metal or metal alloy, regardless of form, that can be ignited and react over the whole length of a sample in 10 minutes or less, when tested in accordance with the UN Manual of Tests and Criteria.

§ 173.125 CLASS 4 - ASSIGNMENT OF PACKING GROUP.

(a) The packing group of a Class 4 material is assigned in column (5) of the § 172.101 Table. When the § 172.101 Table provides more than one packing group for a hazardous material, the packing group shall be determined on the basis of test results following test methods given in the UN Manual of Tests and Criteria (IBR, see § 171.7 of this subchapter) and by applying the appropriate criteria given in this section.

(b) Packing group criteria for readily combustible materials of Division 4.1 are as follows:

(1) (i)Powdered, granular or pasty materials must be classified in Division 4.1 when the time of burning of one or more of the test runs, in accordance with the UN Manual of Tests and Criteria, is less than 45 seconds or the rate of burning is more than 2.2 mm/s.

(ii). Metals or metal alloy-powder, dust, fines, chip, turnings, swarf and sponge must be classified in Division 4.1 when they can be ignited and the reaction spreads over the whole length of the sample in 10 minutes or less.

(2) Packing group criteria for readily combustible materials of Division 4.1 are assigned as follows:

(i) For readily combustible solids (other than metal or metal alloys),

(a) Packing Group II if the burning time is less than 45 seconds and the flame passes the wetted zone.

(b) Packing Group III must be assigned if the burning rate time is less than 45 seconds and the wetted zone stops the flame propagation for at least 4 minutes.

(ii) For readily combustible metal or metal alloys:

(a) Packing Group II must be assigned to any form of metal or metal alloy that can be ignited by a spark, butane torch flame or propane oxygen torch flame and the burning rate over 100 mm is greater than 4 mm/s but less than 30mm/s.

(b) Packing Group III must be assigned to any form of metal or metal alloy if the metal ignites by butane torch flame or propane-oxygen torch flame and the burning rate over 100 mm is less 4 mm/s.

UN MANUAL OF TESTS AND CRITERIA

33.2.4 TEST N.1: TEST METHOD FOR FLAMMABLE SOLIDS

33.2.4.1 INTRODUCTION

The ability of a substance in a pile or layer to propagate combustion is tested by igniting it and determining the burning time. This test method does not identify flash fire and explosion hazards for solids dispersed in air.

33.2.4.2 APPARATUS AND MATERIALS

A mould 250 mm long with a triangular cross-section of inner height 10 mm and width 20 mm is used to form the train for the burning rate test. On both sides of the mould, in the longitudinal direction, two metal sheets are mounted as lateral limitations which extend 2 mm beyond the upper edge of the triangular cross-section (figure 33.2.4.1). If the substance does not conform to the mould, a continuous train of material that is 250 mm x 10 mm x 20 mm is formed. An impervious, non-combustible, low heat conducting plate is used to support the sample train.

33.2.4.3 PROCEDURE

33.2.4.3.1 Screening test

33.2.4.3.1.1 For non-metals, the substance, in its commercial form, should be formed into an unbroken strip or powder train about 250 mm long by 20 mm wide by 10 mm high on a cool, impervious, low heat-conducting base plate. A hot flame (minimum temperature 1000°C) from a gas burner (minimum diameter 5 mm) should be applied to one end of the powder train until the powder ignites or for a maximum of 2 minutes . It should be noted whether combustion propagates along 200 mm of the train within the 2 minute test period. If the substance does not ignite and propagate combustion either by burning with flame or smouldering along 200 mm of the powder train within 2 minutes (or 20 minute) test period, then the substance should not be classified as a flammable solid and no further testing is required. If the substance propagates burning of a 200 mm length of the powder train in less than 2 minutes, the full test programme in 33.2.4.3.2 should be carried out.

33.2.4.3.1.2 For metal and metal-alloys, the substance, in its commercial form and particle size ranges, should be formed into an unbroken strip or continuous train about 250 mm long by 20 mm wide by 10 mm high on a cool, impervious, low heat-conducting base plate. A propane-oxygen torch flame (minimum temperature 1650°C) should be applied to one end of the train until the material ignites or for a maximum of 2 minutes. It should be noted whether ignition occurs or if combustion propagates by flame, glowing, or smoldering any distance after the ignition source is removed. If the substance does not ignite and propagate combustion either by burning with flame or smoldering along 200 mm of the powder train within 20 minutes, then the substance should be sieved and the finest particle size formed into a continuous train, exposed to the same ignition source, and monitored for propagation of burning by glowing, flames, or smoldering. If both preliminary screening tests do not result in ignition or flame spread greater than 20 mm from the ignition source, the material should not be classified as a flammable solid; no further testing is required. If the commercial form or finest fraction of substance propagates burning greater than 20 mm length of the unbroken strip or continuous train, the full test programme in 33.2.4.3.2 should be carried out.

33.2.4.3.2 BURNING RATE TEST

33.2.4.3.2.1 The substance, in the commercial form and particle size ranges, should be loosely filled into the mold. The mold is then dropped three times from a height of 20 mm onto a solid surface. The lateral limitations are then removed and the impervious, non-combustible, low heat conducting plate is placed on top of the mold, the apparatus inverted and the mold removed. Pasty substances are spread, turnings and swarf are formed on a non-combustible surface in the form of a rope 250 mm in length with a cross section of about 100 mm^2. In the case of spherical powder metals that do not maintain a triangular material train, a similarly sized trough with a triangular cross section is used. In the case of a moisture sensitive substance, the test should be carried out as quickly as possible after its removal from the container. The pile should be arranged across the draught in a fume cupboard. The air speed should be sufficient to prevent fumes escaping into the laboratory and should not be varied during the test. A draught screen may be erected around the apparatus. Additional eye protection is required for metals and metal-alloys that burn brightly.

33.2.4.3.2.2 For substances other than metal and metal alloys that are covered in 33.2.4.3.2.4, 1 ml of a wetting solution should be added to the pile 30 – 40 mm beyond the 100 mm timing zone. Apply the wetting solution to the ridge drop by drop, ensuring the whole cross-section of the pile is wetted without loss of liquid from the sides. The liquid should be applied over the shortest possible length of the pile consistent with avoiding loss from the sides. With many substances, water rolls off the sides of the pile, so the addition of wetting agents may be necessary. Wetting agents used should be free from combustible diluents and the total active matter in the wetting solution should not exceed 1%. This liquid may be added to a hollow up to 3 mm deep and 5 mm in diameter in the top of the pile.

33.2.4.3.2.3 Any suitable ignition source such as a small flame or a hot wire of minimum temperature 1000 C is used to ignite the pile at one end. When the pile has burned a distance of 80 mm, measure the rate of burning over the next 100 mm. For substances other than metal powders, note whether or not the wetted zone stops propagation of the flame for at least 4 minutes. The test should be performed five times using a clean cool plate each time, unless a positive result is observed earlier.

33.2.4.3.2.4 For metal and metal alloys, the substance is tested in the as-received condition including particle size range, moisture content, and chemical mixture (if not pure, including cutting fluid residues).

33.2.4.3.2.5 For metal and metal alloys, the substance is exposed to a butane torch flame with a temperature greater than 1000°C at one end of the train for 3 minutes. If ignition occurs, the burning rate is recorded as in 33.2.4.3.2.3. If ignition does not occur after 3 minutes, a propane-oxygen torch flame is applied to the other end of the same train for 1 minute. If ignition occurs, the burning rate is recorded as in 33.2.4.3.2.3. If ignition occurs with a butane torch flame, an optional test has sparks from a flint-style igniter repeatedly directed at the material train for 2 minutes to determine if ignition can occur by spark.

33.2.4.3.2.6 For cutting fluid and metal and metal alloys submerged in water, the metal or metal-alloy should be tested per 33.2.4.3.2.5 after washing and drying and classified based on the higher hazard condition.

33.2.4.4 TEST CRITERIA AND METHOD OF ASSESSING RESULTS

33.2.4.4.1 Powdered, granular or pasty substances should be classified as flammable solids when the time of burning of one or more of the test runs, in accordance with the test method described in 33.2.4.3.2, is less than 45 s or the rate of burning is more than 2.2 mm/s.

33.2.4.4.2 For flammable solids (other than metal powders), packing group II/Category 1 should be assigned if the burning time is less than 45 s and the flame passes the wetted zone.

33.2.4.4.3 For flammable solids (other than metal powders), packing group III/Category 2 should be assigned if the burning time is less than 45 s and the wetted zone stops the flame propagation for at least four minutes.

33.2.4.5 TEST CRITERIA AND METHOD OF ASSESSING RESULTS FOR METALS AND METAL ALLOYS

33.2.4.5.1 Packing group II/Category 1 should be assigned to metal or metal alloys that ignite by a butane torch flame (T>1000°C) or propane oxygen torch flame (T>1650°C) and the zone of reaction spreads 100 mm along the sample in 3 to 25 seconds.

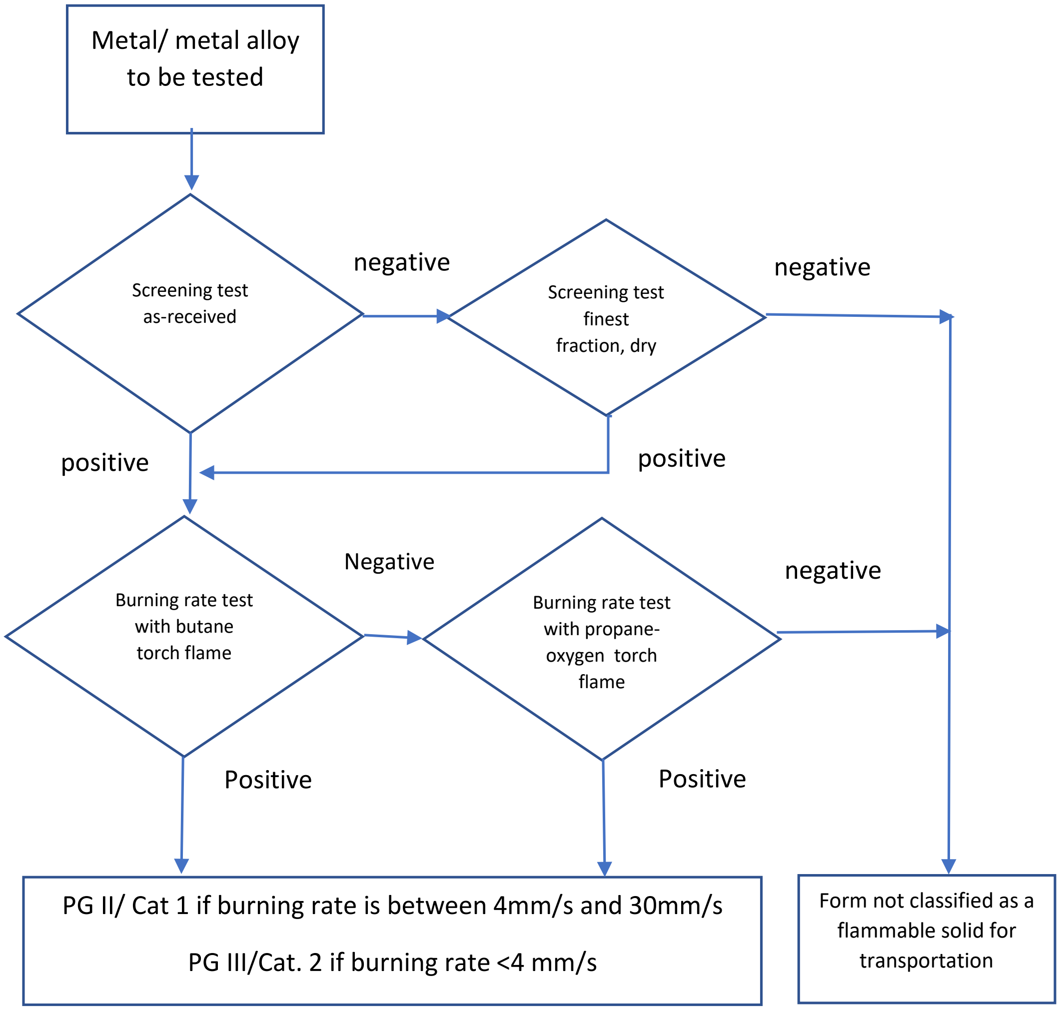
33.2.4.5.3 Packing group III/Category 2 should be assigned to metal or metal alloys if a butane torch or propane-oxygen torch flame ignites the substance and the reaction spreads 100 mm along the sample in more than 25 seconds.

33.2.4.5.4. A not readily combustible solid of Division 4.1 is assigned to metal or metal alloys that may glow but does not ignite from a propane-oxygen torch flame and the reaction does propagate away from the location of the ignition source.

33.2.4.6 EXAMPLES OF RESULTS

Substance (other than metals and metal alloys)	Preliminary burning time (s)	Burning time (s)	Delay time (s)	Result
Manganese ethylene Bis (dithiocarbanate) Complex with zinc salt 88%(Mancozeb)	-	102	-	Not a flammable solid
Manganese ethylene bis (dithiocarbamate) complex with zinc salt 80% (Mancozeb)	-	145	-	Not a flammable solid
Manganese ethylene bis (dithiocarbamate) Complex with zinc salt 75% (Mancozeb)	No ignition	-	-	Not a flammable solid

Substance	Ignition source	Burning rate (mm/s)	Classification
Titanium powder (-270+500 mesh)	Butane torch flame	1.6	PG III
Titanium chip	Propane-oxygen torch flame	1.8	PG III
Magnesium chip (>99%, 4-30 mesh)	Butane torch flame	0.2	PG III
Zirconium fines, dry	Spark, butane torch flame	5.3	PG II


Metal/ metal alloy to be tested
Screening test as-received
negative
Screening test finest fraction, dry
negative
positive
positive
Burning rate test with butane torch flame
Negative
Burning rate test with propane-oxygen torch flame
negative
Positive
Positive
PG II/ Cat 1 if burning rate is between 4mm/s and 30mm/s
PG III/Cat. 2 if burning rate <4 mm/s
Form not classified as a flammable solid for transportation

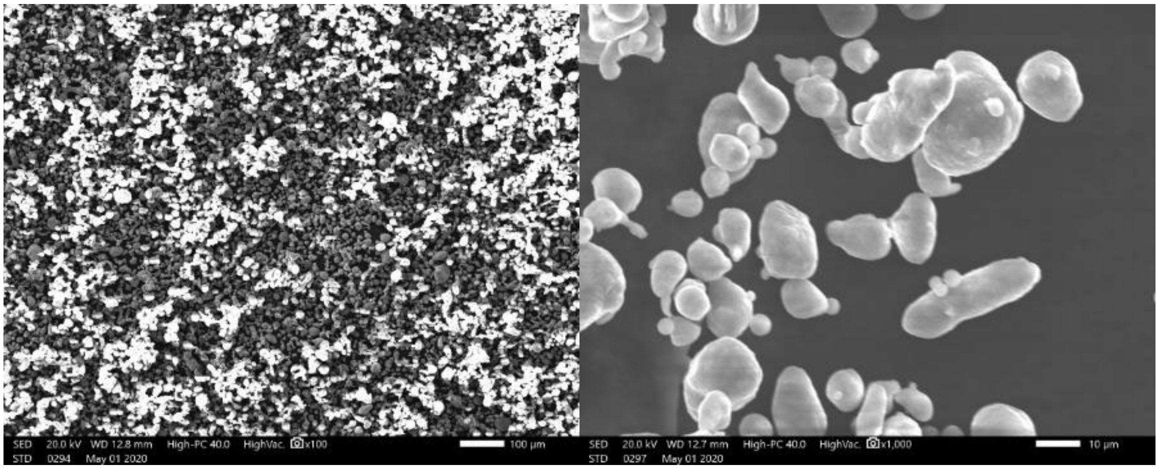
APPENDIX 2. DETAILED DESCRIPTION OF BENCH-SCALE TESTING WITH METALS AND METAL ALLOYS

Various metal, metal-alloys, and metal-containing mixtures were subjected to characterization and testing using the proposed test method. The metals and test results are listed in alphabetical order.

ALUMINUM [CAS 7429-90-5]

Aluminum (Al, >99%) powder was purchased from Sigma Aldrich (Lot No. MKBL891V). The powder had a uniform appearance, was light gray in color, and free flowing. SEM images of the powder, described as spherical with diameter less than 30 microns, at 100 and 1,000 times magnification are shown in Figure A2-1. The particles are smooth, roughly spherical with minor agglomeration tendency.

Figure A2-1 SEM images of aluminum powder



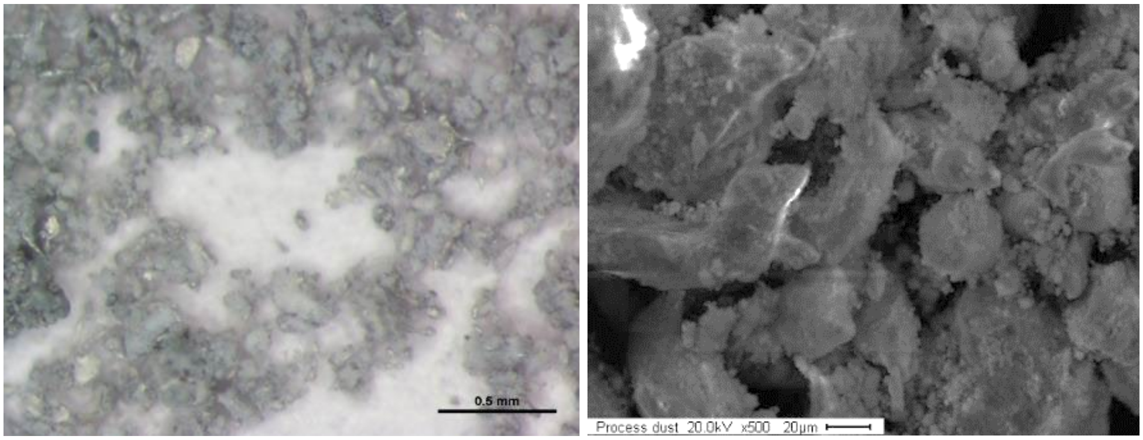
When formed into a continuous train on a cool ceramic plate, the aluminum powder did not ignite when exposed to a butane torch flame for 180 s. When exposed to a propane-oxygen torch flame, the material melted and locally ignited with a corresponding bright glow but extinguished as soon as the torch flame was removed.

ALUMINUM PROCESS DUST

Aluminum dust was collected from a dust collector associated with a plasma torch cutting operation (Figure A2-2). Stereomicroscope and SEM images of the dust are shown in Figure A2-3. The light gray, fine dust was analyzed by EDS and found to contain 40 wt% aluminum (Al), 43% oxygen (O), and 17% carbon (C). Moisture content was less than 1 wt%. When formed into a prismatic train, the material did not ignite when exposed to a butane torch flame. When exposed to a propane-oxygen torch flame, the material ignited and was bright glowing, but combustion was not sustained.

Figure A2-2 Indoor dust collector associated with plasma cutting operation

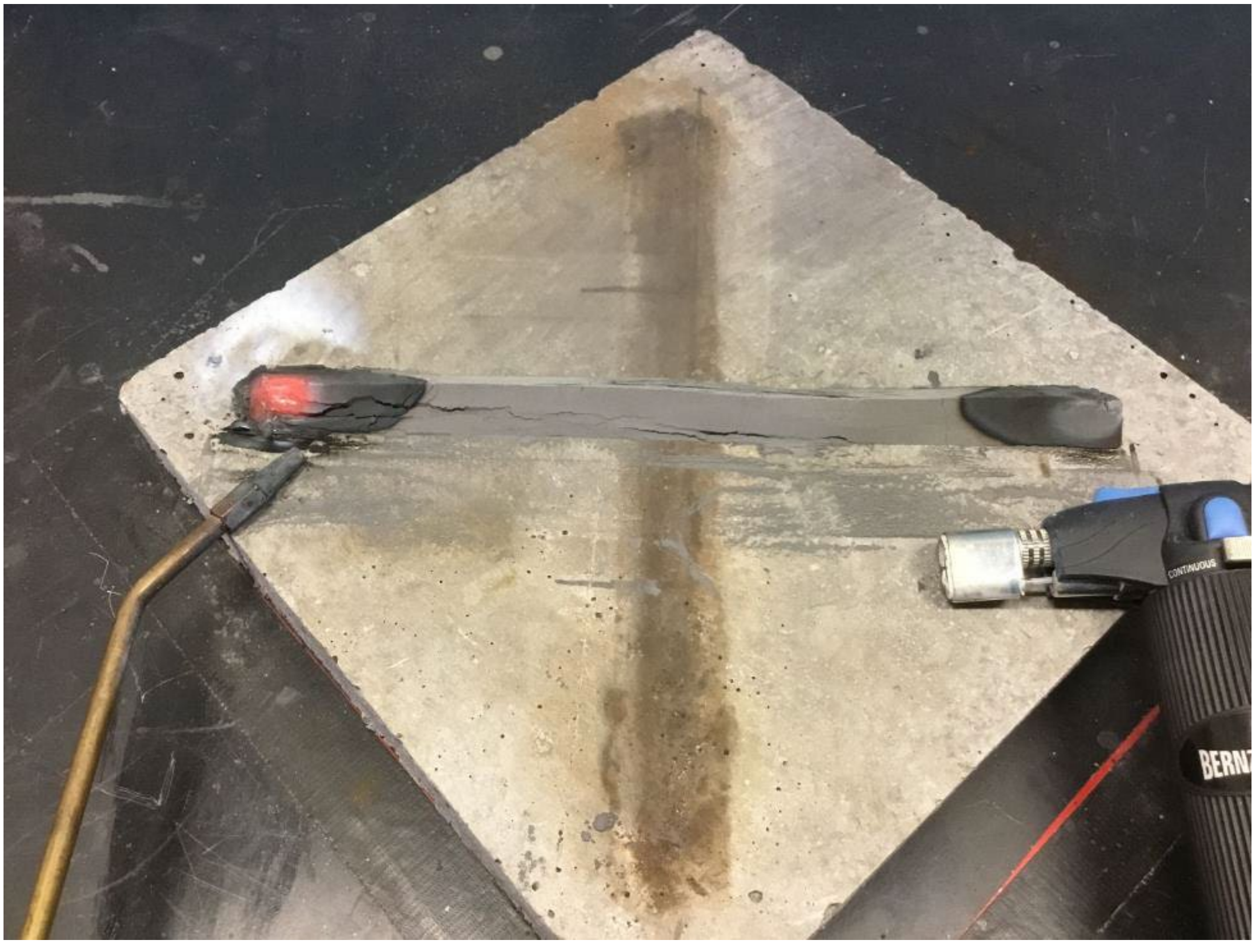
Figure A2-3 Aluminum-based particulate from dust collector receptacle



IRON [CAS 7439-89-6]

Iron (Fe, 97%) powder was purchased from Sigma Aldrich (-325 mesh)[19]. The powder was received in a plastic container under inert gas. The container label displayed a flammable solid symbol. The iron powder was gray, homogeneous, and had a very fine particle size (e.g., dust-like). The moisture content was less than 1 wt%. When formed into a prism on a ceramic plate and exposed to a butane torch flame and then a propane-oxygen torch flame for 180 s and 90 s, respectively, ignition did not occur (Fig. A2-4).

Figure A2-4 Iron powder



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[19] Lot No. STBJ0239, PCode 102103242

IRON-RICH (STEEL) PROCESS DUST

Very fine, brown particulate solid or dust from a steel process was received for analysis. The average dust composition was 78 wt% iron (Fe) with 9 wt % oxygen (O), 7 wt% carbon (C), 4 wt% manganese (Mn) and 2 wt% zinc (Zn). An EDS spectrum is shown in Figure A2-5. The dust was formed into a prismatic train on a cool ceramic plate. A butane torch flame applied to one end for 120 s was sufficient to initiate smoldering combustion of the iron-rich mixture with very minor gaseous products evolving. Smoldering was observed as discoloration spreading over the surface. Elevated temperatures were recorded as the smoldering front passed over the two K-type thermocouples embedded in the material. The average burning rate was **0.40±0.07 mm/s**. Peak temperatures were 440±43°C. Figure A2-6 is a representative image of the powder train with smoldering combustion.

Figure A2-5 SEM image at 1000x magnification and EDS spectrum of steel process dust

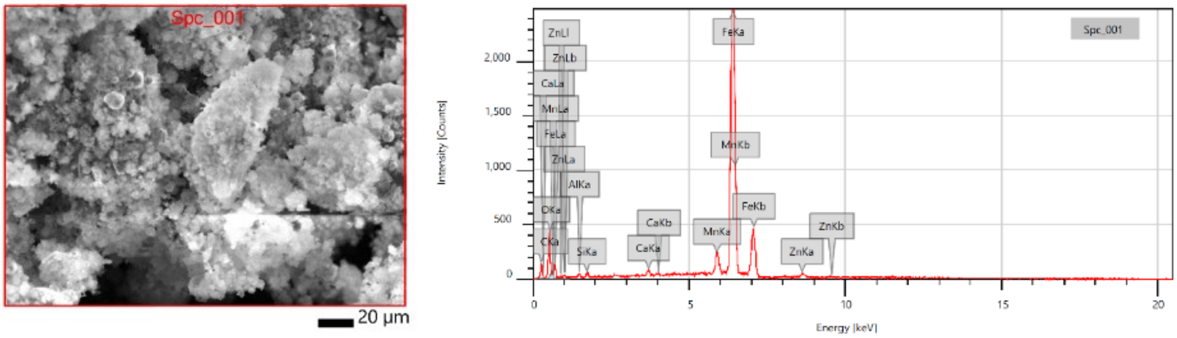


Figure A2-6 Smoldering steel process dust. The blue arrow indicates the smoldering front

MAGNESIUM [CAS 7439-95-4]

Magnesium chip (Mg, >99%) was procured from Sigma Aldrich. The listed particle size range was 3 to 40 mesh or 0.5 to 5 mm. The burning rate of the lustrous silver-appearing particulate as a prismatic train was compared to the burning rate in a trough with the same dimensions as the prismatic train. A butane torch flame was required to ignite the metal. Once ignited, the metal burned with a bright, white glow. The results of magnesium chip burning rates in a trough and prism are summarized in Table A2-1.

Table A2-1 Burning rate of magnesium chip

Configuration	Peak temperature (degree C)	Burning rate (mm/s)
Prism	967	0.26
Trough	984	0.20

MANGANESE [CAS 7439-96-5]

Manganese (Mn, >95%) is a transition metal element. Two sources of manganese were subjected to analysis and testing. One source of manganese was commercial (Fig. A2-7); the second was a process dust (Fig. A2-8). The commercial source of manganese powder consisted of discrete, rock-like, free-flowing, tan or brown colored particles with diameters ranging from 116 to 262 microns; average particle dimension was 164±44 microns. The average composition was 95% manganese (Mn) with 5% oxygen (O) and/or carbon (C). The process dust was reddish in color and had high surface area.

Figure A2-7 Commercially available particulate manganese (95%, -100+140mesh)

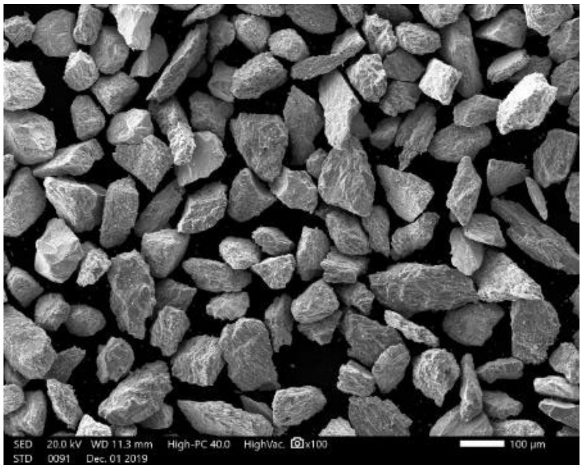
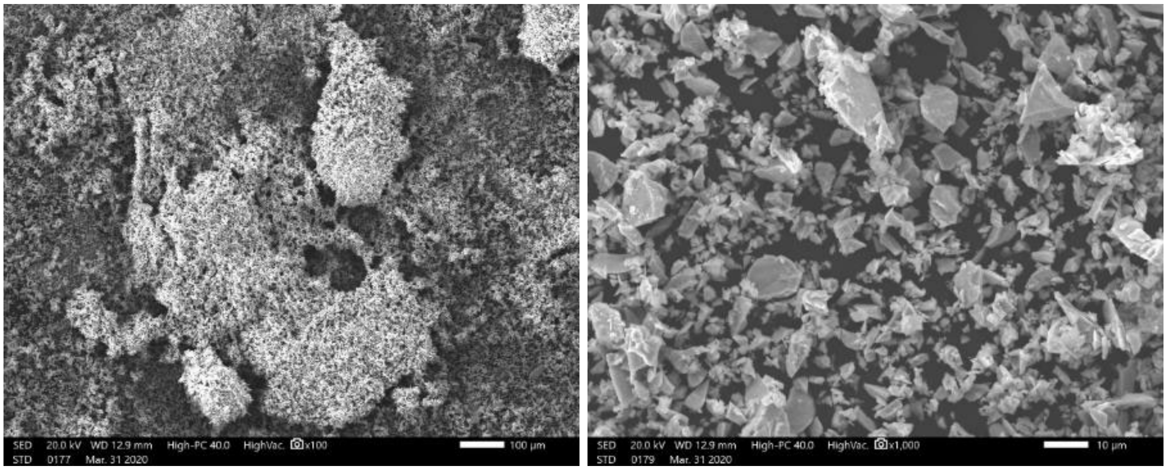


Figure A2-8 Manganese process dust at 100 x (left) and 1000 x (at right) magnification.

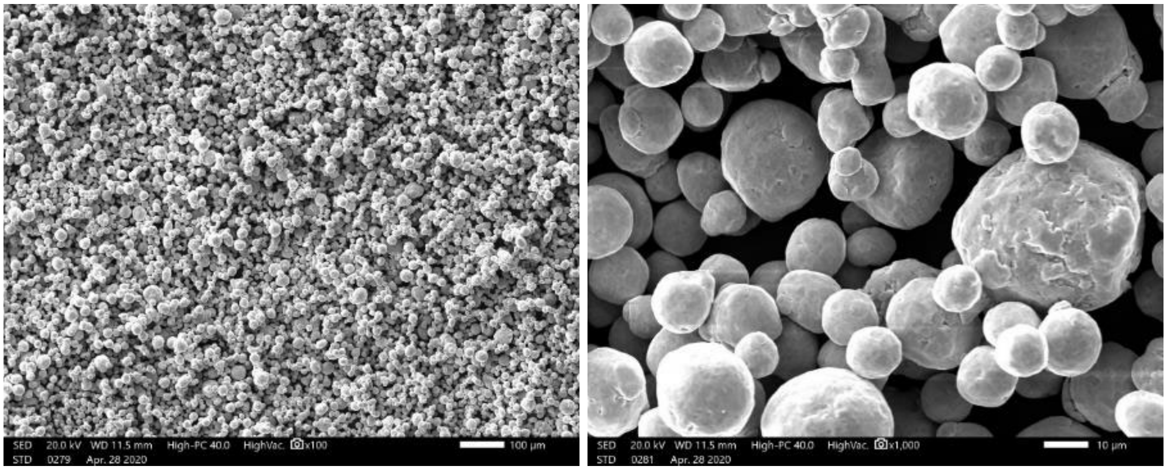


Neither the manganese process dust or angular particulate material ignited when exposed to a butane torch flame for 180 s or a propane-oxygen torch flame for 60 s at the other end.

NICKEL [CAS 7440-02-0]

Nickel (Ni) powder was purchased from a commercial source; the packaging was documented. The powder was homogenous and light gray in color. SEM images are shown in Figure A2-9. The particles were discrete and generally round.

Figure A2-9 Particulate nickel



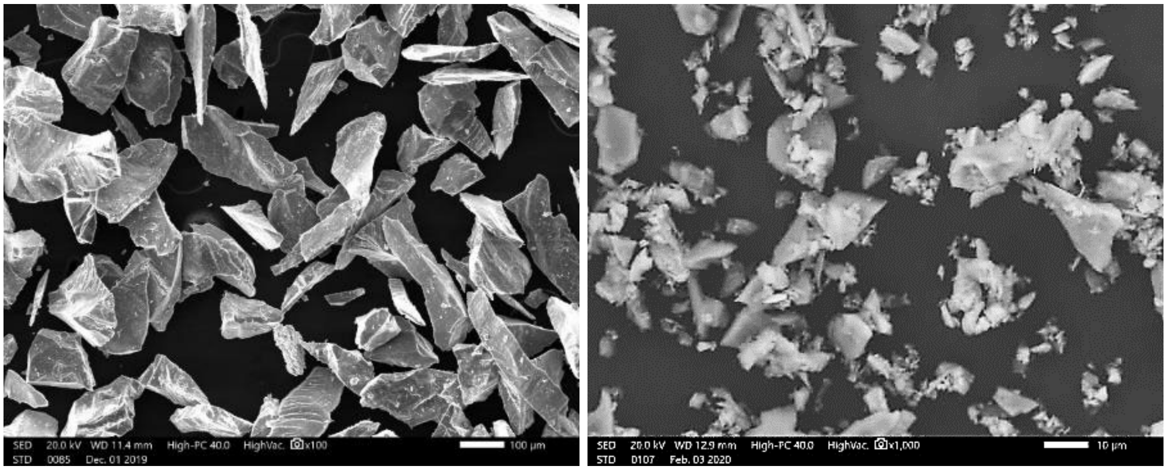
The nickel powder did not ignite when exposed to a butane torch flame for 180 s or a propane-oxygen torch flame for 60 s (Fig A2-10).

Figure A2-10 Nickel powder did not ignite from butane or propane oxygen torch flames

SILICON [CAS 7440-21-3]

Two sources of silicon (Si, >94%) were procured for testing. According to Bretherick's, finely powdered silicon is explosible and a possible thermite pair with metal oxides. Both sources of silicon were commercially available. Representative SEM images of the two particulate samples are shown in Figure A2-11—note the order of magnitude difference in magnification. The particle shape for both sources was angular.

Figure A2-11 Two commercially available particulate silicon samples



The powder (99%, -325mesh) was formed into a 250 mm prismatic train on a ceramic plate. The silicon did not discolor or ignite when exposed to the butane torch flame for 180 s. The silicon powder ignited when a propane-oxygen torch flame was applied; combustion propagated a short distance then extinguished. Similar observations were made with the second commercial source with larger angular particles; however, ignition, following exposure to the propane oxygen torch flame, even briefly, did not occur.

TANTALUM ALLOY (TA-2.5W)

A tantalum alloy powder (Ta-2.5% W)[20] was characterized and subject to testing. The powder particles were spherical (Fig. A2-12). The reported particle size range was -70 to +270 mesh or 59 to 183 microns in diameter. The material was not an admixture. The moisture content of the free-flowing powder was 0.1 weight percent. The powder could not retain the shape of a prism when formed using the mold; the particles spread away from the 10 mm base. As such, a butane torch flame was applied to one end for 300 s. The powder did not ignite, sustain, or propagate combustion. When a propane-oxygen torch flame was applied to the other end of the train; the material ignited locally but did not sustain or propagate combustion (Figure A2-13). When the torch was removed, any glowing ceased. The same material was poured into a trough with the same dimensions as the mold with the same results—no ignition (Fig. A2-14).

Figure A2-12 Tantalum 2.5% W alloy powder

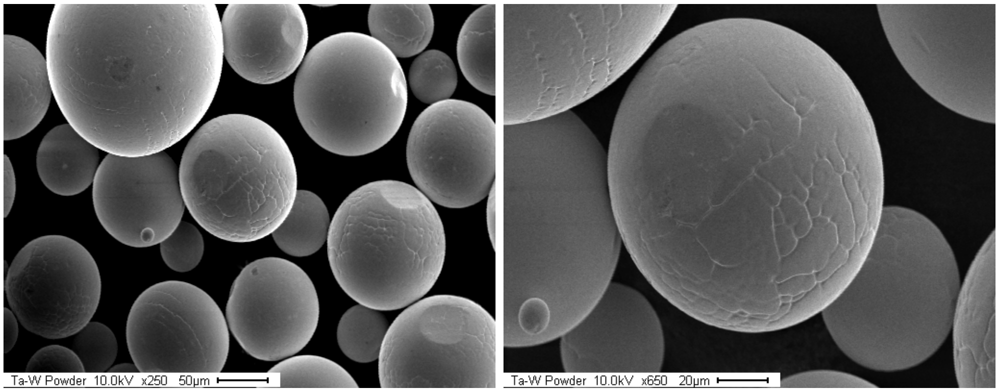


Figure A2-13 Ta-2.5W exposed to butane and propane-oxygen torch flames-no ignition

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[20] Timet, Ta-2.5W (-70+270 mesh), Lot No. 2X1500358

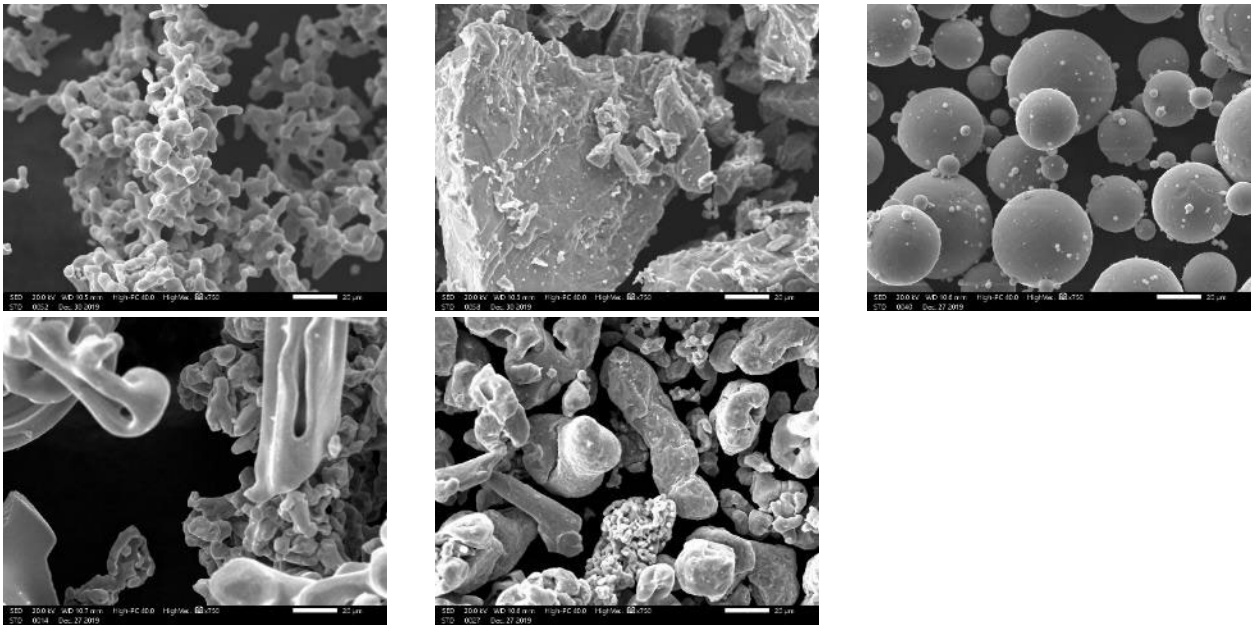
Figure A2-14 Ta2.5W powder in a trough – no ignition

Titanium metal can have different alloy compositions and forms, both in large quantities. The raw form of titanium is rutile (TiO_2), which is chemically treated and reduced to titanium metal in the form of irregular sponge. Titanium metal is also reclaimed and/or recycled. Reclamation can involve sorting by chemistry and size. Large and small particulate is subject to washing, drying, and comingling for melting in industrial furnaces then cast into ingots of specific chemistry. Scrap metal can range in size from large sheets after stamping to larger cuttings to fines and turnings. The resulting ingots are further processed by various machining operations into round and other solid stock for traditional manufacturing. New manufacturing methods including powder metallurgy and additive manufacturing will use powder form titanium and titanium alloy starting materials.

SMALL PARTICLES

Discrete particles of titanium range from powder and dust to fines to chip and flake. The ignition propensity and burn rate of the various small particle titanium were determined. The range in shape and surface area of titanium powder and dust particles are represented in Figure A2-15. The morphology ranged from high surface irregular, angular, spherical, and dust particles.

Figure A2-15 Forms of titanium powder and dust



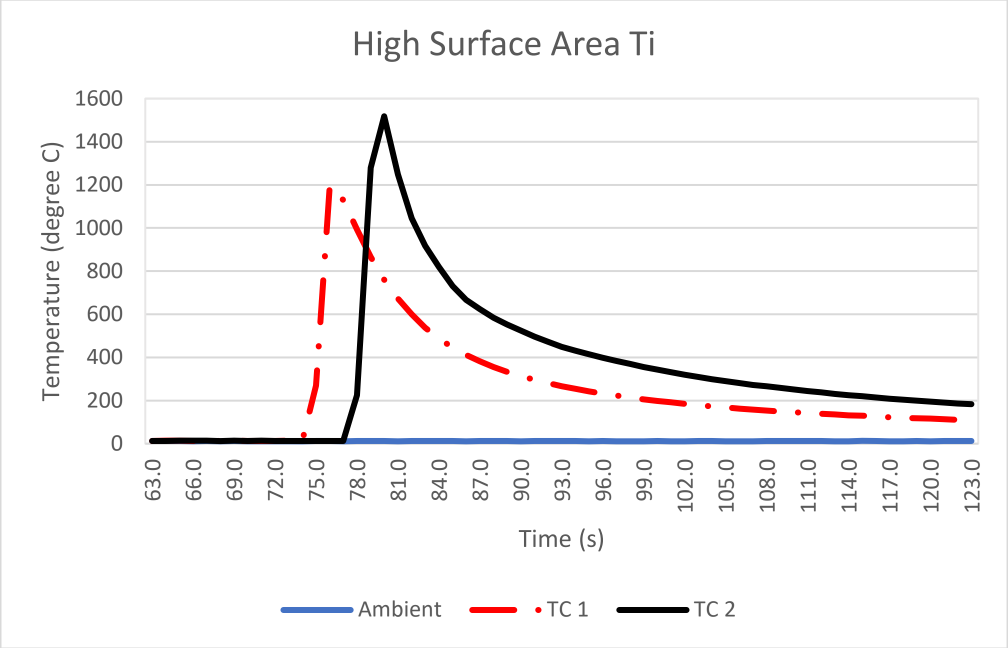
Particle size distributions from sieve of some particulate metal are summarized in Table A2-2, reported according to ASTM B214-16 Standard test method for sieve analysis of metal powders.

Table A2-2 Particle size distribution of small particle titanium

Particle size	Sieve No.	Ti-5Al Dust %By Mass	TiVAl Fines Source 1 %By Mass	Ti6V6Al Fines Source 2 %By Mass
>3.35mm	+6	0.0	0.2	12.5
≤3.35>2mm	-6+10	0.0	3.9	**33**
≤2mm>1mm	-10+18	0.0	**55**	**46.3**
≤1mm>500um	-18+35	0.0	**38**	6
≤500um>300um	-35+50	5.3	2.6	0.6
≤300um>150um	-50+100	**55.5**	0.1	0.5
≤150um>90um	-100+170	18.2	Trace	Trace
≤90um>63um	-170+230	9.2	Trace	Trace
≤63um>45um	-230+325	6.7	Trace	Trace
≤45um	-325	4.8	Trace	trace

A typical temperature profile of burning titanium is shown in Figure A2-16. The thermocouples were spaced 100 mm apart. Table A2-3 is a summary of particulate titanium and titanium alloy powder test results. The titanium particulate[21] with very high surface area ignited readily by spark and had the fastest burning rate.

Figure A2-16 Temperature profile of burning titanium



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[21] Armstrong

Table A2-3 Summary of titanium and titanium alloy powder test results

Composition	Form	Particle Size (mesh)	Ignition source (PO=propane oxygen torch flame)	Burning Rate (mm/s)
Ti 8%Al 1%Mo1%V	Spherical powder	-60+100	Butane torch then PO	-
		-100+325	Ignites by PO torch but does not propagate	-
		-325	Ignites by PO torch but does not propagate	-
Ti (CP2)	Spherical powder	nr	Ignites by PO torch	0.4
Ti 6%Al 4%V	Powder	-270	Ignites by PO torch	0.7
Ti 6%Al 2%Sn 4%Zr 2%Mo	Spherical powder	-60+100	Ignites by PO torch but does not propagate	-
		-100+325	Ignites by PO torch but does not propagate	-
		-325	Butane torch DNI; ignites by PO torch	1.3
Ti	Spherical powder	-270+500	Butane torch	1.6
Ti 4%V 5%Al 2%Fe	Fines, clean, dried	nr	Butane torch DNI; ignites by PO torch	2.0-3.2
Ti 5%V 3%Al	Fines	-35	Butane torch DNI; ignites by PO torch	3.2
		-35+50	Butane torch DNI; ignites by PO torch	5.1
		-50+100	Butane torch DNI; ignites by PO torch	5.7
97% Ti (HDH)		-60	Spark	4.2
Ti	Angular particles	-325	Spark	5.6
		-40	Burning metal	5.9
		+20	Burning metal	5.1
Ti 5%Al	Fines, rectangular	-50+325	Spark	7.1
Ti	High surface area dust	-100	Spark	38.1

Trials with various titanium-rich particulate were performed as a prism and trough. The burning rate for Ti-5Al, as a prism, was 6.6 mm/s, while the burning rate in the trough with the same dimensions was 7.5 mm/s. Titanium powder (-100+325 mesh) burning rates were 0.87 mm/s as a prism and 0.80 mm/s in a trough. HDH -60 mesh particulate burned 4.2 mm/s as a prism and 2.6 mm/s in a trough.

CHIP (FINE AND COARSE)

Two sizes of titanium-rich chip, fine and coarse, were compared. The source of Ti chip was dryer fines. From inspection, the chip appeared to be washed. The surface of the chip was serrated, as shown in Figure A2-17. One end of a prismatic train of fine chip when exposed to a butane torch flame for 180 s did not ignite but did ignite when exposed to a propane oxygen torch flame for less than 10 s. The burning rate was 1.8 mm/s. The same ignition propensity was exhibited in the trough; the burning rate however was slower at 1.4 mm/s. Coarse chip (Ti8V2Al) ignited locally but did not spread when exposed to a butane torch flame, propane-oxygen torch flame, or burning metal.

Fine and coarse chip were used in the branches of a double cross trough; titanium dust (an ultra-fine chip) was used in the main branch (Fig. A2-18). The titanium dust ignited readily, and the propagated burning resulted in the ignition of the branch with fine chip. The coarse chip, as mentioned previously, ignited locally but did not propagate. From temperature data, the burning rate of the titanium dust was 7.1 mm/s, and the fine chip was 1.6 mm/s. Figure A2-19 is a thermal image of the double-cross trough test.

Based on the results of the burn rate test with only the butane torch flame, the fine chip would not be classed as a Division 4.1 flammable solid (false negative). The coarse chip ignites but resists spreading burning from particle to particle.

Figure A2-17 Fine and coarse chip

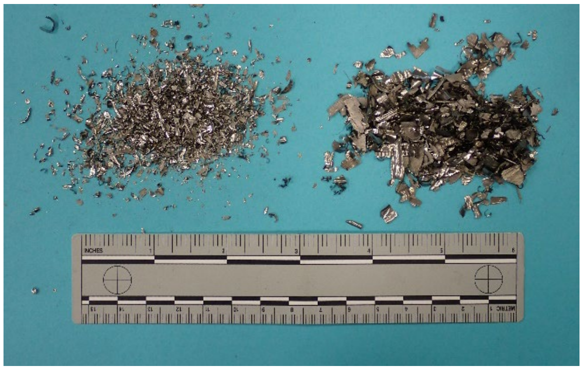


Figure A2-18 Double cross trough with Ti5Al dust in main branch, fine and coarse Ti chip in branches

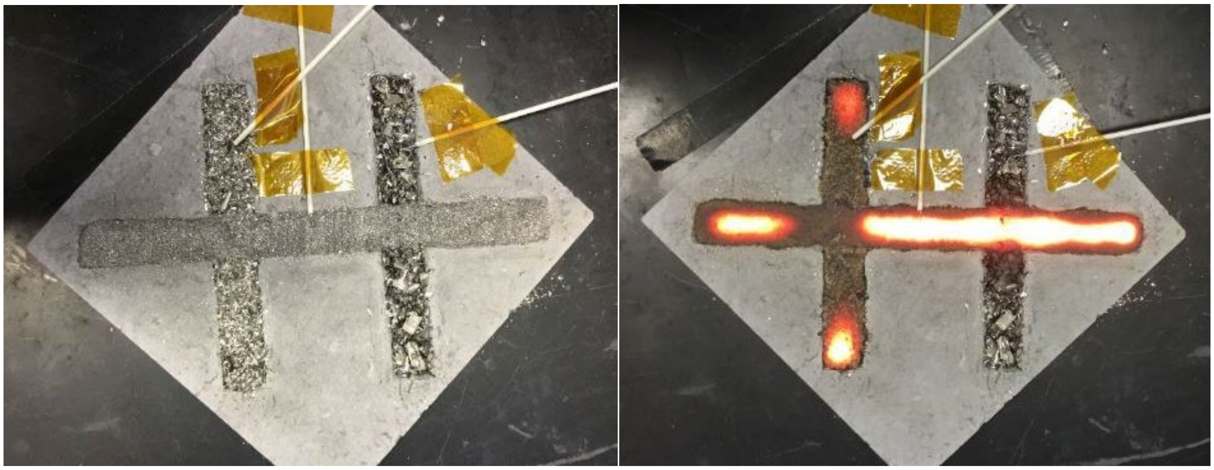
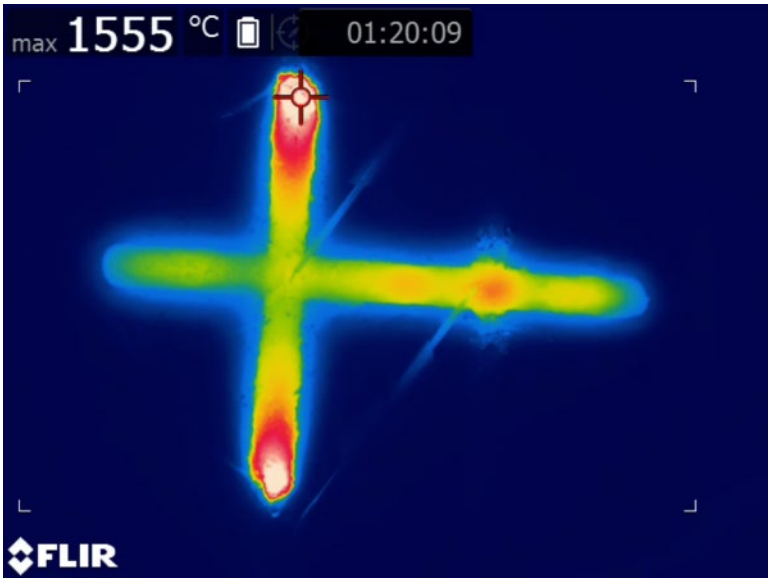


Figure A2-19 Thermal image of the double cross trough of test shown in Figure A2-18



The instrumented double cross trough illustrates the difference in burning rate and the regular rate of travel. The distance traveled by the burning titanium dust between TCs was 100 mm; the distance traveled by the burning fine chip between TCs was 70 mm. The burning rate of titanium dust was 8.3 mm/s compared to 1.5 mm/s for the fine chip. The coarse chip in the second branch locally ignited, as demonstrated by the increase in temperature on either side of the main branch, but burning was not sustained.

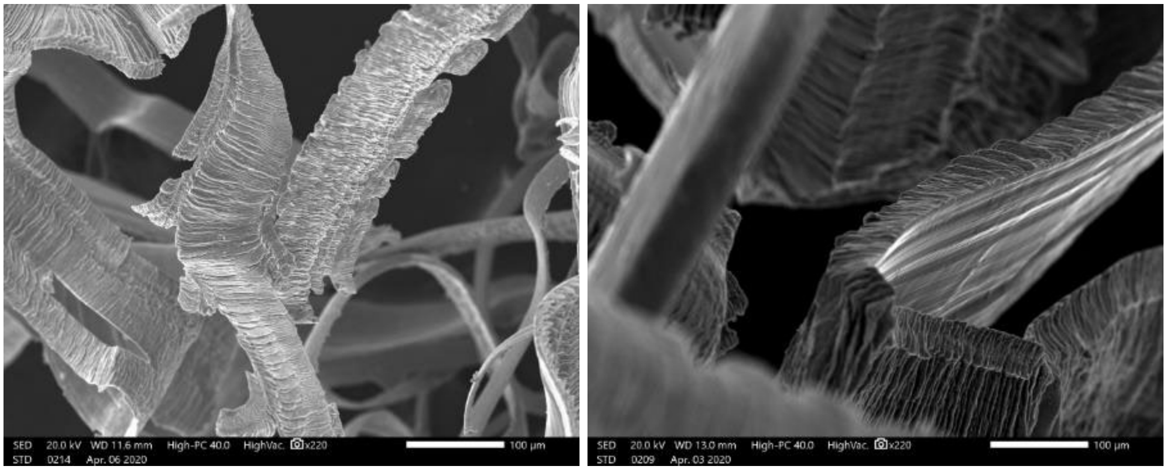
TURNINGS

Coarse and fine titanium-rich turnings were evaluated. The very fine turnings are also known as swarf. Both are the result of secondary process operations, and both have the consistency of Brillo-type pads. Both the fine and very fine turnings were brittle, and handling resulted in the creation of finer particles. The as-received fine turnings had residual cutting fluid; the fines were rinsed with hot water and minor detergent then dried in a laboratory oven at 100°C for at least 60 minutes. Similarly, a swarf was received submerged in water. Swarf was dried in the oven at 100°C for at least 60 minutes. The fine and very fine turnings consisted of machined particles with a long axis.

FINE TURNINGS

Fine turnings and swarf are compared at the same magnification in Figure A2-20.

Figure A2-20 SEM Images of swarf (left) and fine turnings (right)



A trough was filled with dry fine turnings, and a butane torch flame was applied to one end. Once ignition occurred, the titanium burned with a bright glow. In the first test, the fines self-extinguished. Four trials were performed with the material as a prismatic train. In four trials, ignition occurred and propagated the full length. In the final trial, the materials self-extinguished after 105 mm. Figure A2-21 compares the temperature profiles from three trials with fine turnings showing good reproducibility.

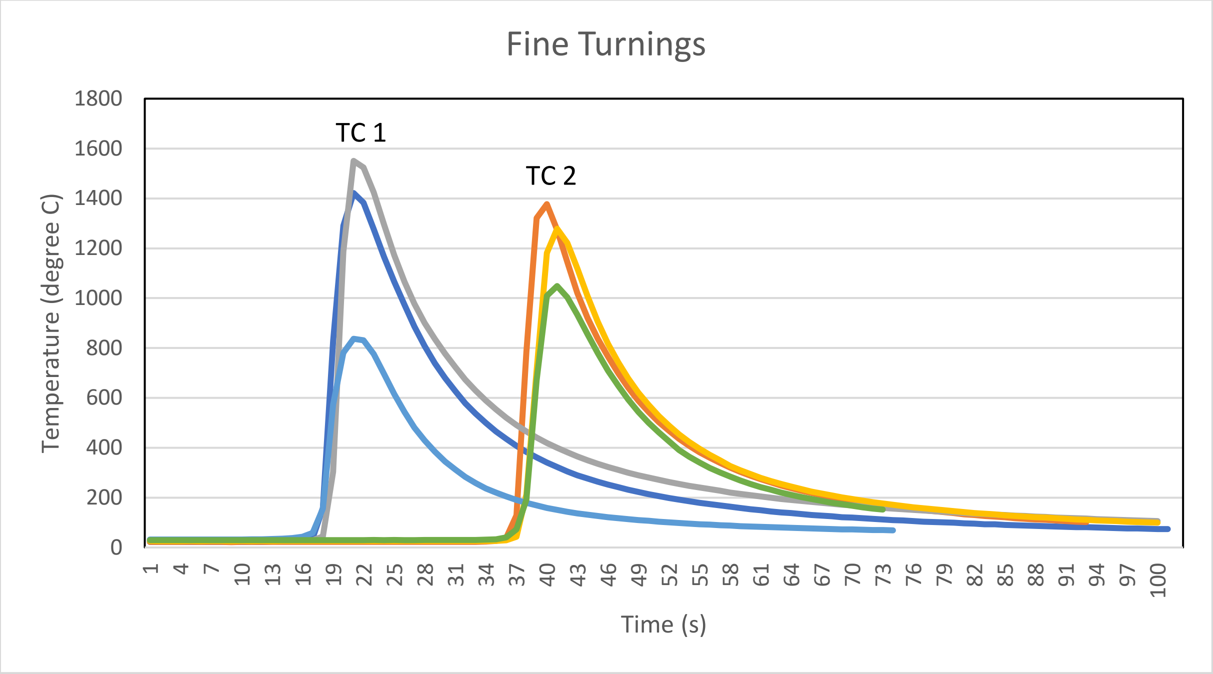
A second source of fines (saw fines) from one supplier was subject to testing before (as-received) and after washing with dish soap, rinsing and drying. The material as-received was coated, not submerged in cutting fluid. After drying, the turnings were formed into a continuous train, exposed to a butane torch and the burning rate recorded. One of the five trials utilized the mold to compare the results with material formed without a mold. The clean, dry saw fines were ignited readily using a butane torch flame; localized ignition occurred with sparks but were not sustained. The metal burned erratically but continuously with an orange flame above the pile and bright burning within the pile. Burning duration was recorded when the bright burning crossed the 100 mm markers. The burning rate over 100 mm ranged from 3.8 to 5 mm/s or 19.8 to 26 s; the average of five trials was 4.3 mm/s. The burning duration of fines that were formed using the mold was 22 s which was within the range of burning duration of the material formed into a continuous 250 mm train which ranged from 19 s to 26 s on the test plate.

SWARF

The titanium swarf from a machining process as-sampled was fully submerged in water. The swarf was dark gray and resembled a very fine Brillo-pad material. The swarf was dried in a laboratory oven to less than 1 weight percent moisture then formed into a prismatic train by packing the material into a mold. The dry titanium swarf was frangible and would break into small particles upon handling. The burning rate of dry swarf compared to swarf with different loadings of moisture or water was examined.

Dry swarf and swarf with up to 33 wt% moisture content was readily ignited using a spark from the flint-style spark igniter directed at one end of the prism. Swarf with low moisture burned with increased orange-yellow flame compared to dry swarf and ejected sparks from the train as it burned. When squeezed of residual water from the sample container, formed into a prism, and then exposed to a butane torch on one end for 180 s and a propane oxygen torch on the other end for 60 s, ignition did not occur. The results of testing swarf with different levels of moisture are summarized in Table A2-4.

Figure A2-21 Three temperature profiles from fine turnings



Both the turnings, when dry, were readily ignited and spread combustion.

Table A2-4 Variation in burning rate based on moisture content

Form	Stopwatch time (s)	Burn rate (mm/s)
Dry swarf (prism)	6	16.6
Swarf with 24wt% moisture	9	11.1
Swarf with 33wt% moisture	12	8.3
Wet	NI	NA

LARGE PARTICLES

Larger particles of titanium are typically referred to as rock or sponge. Individual rocks can be ignited. Intimacy in contact between two or more rocks dictates if a burning rock can transfer energy to the adjacent rock to result in propagation.

TITANIUM-SALT ADMIXTURES

Two titanium dust-sodium chloride[22] admixtures were prepared. The 3:1 and 9:1 titanium-salt admixtures were prepared on a volume, not mass, basis. The main branch of a double-cross trough was filled with titanium dust; the two branches contained an admixture. The main branch was ignited with a butane torch in less than 30 s; the burning metal ignited the 9:1 mixture, which propagated in two directions away from the main branch. The 3:1 mixture showed local ignition with bright burning, but combustion failed to propagate and consistently in both directions away from the main branch. The results are summarized in Table A2-5. Additional tests could be performed to determine the minimum concentration of salt required to render a combustible metal difficult to ignite and slower to spread, if ignited.

Table A2-5 Titanium and titanium-salt mixtures

Form	**Burn rate (mm/s)**
Titanium dust (No NaCl)	5
90vol %Ti-10vol %NaCl (9:1)	2.5
75 vol% Ti-25vol% NaCl (3:1)	NI

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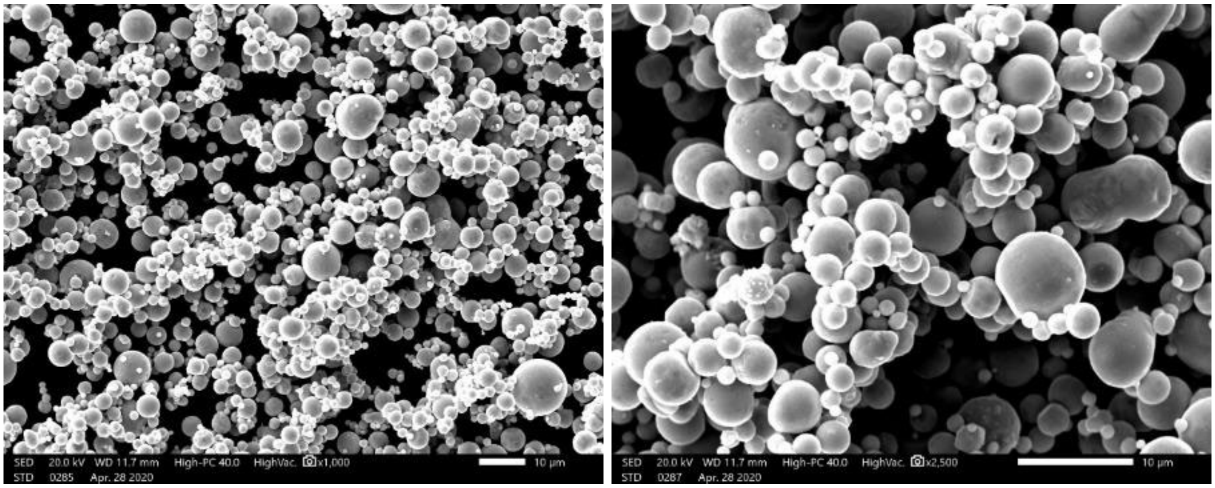
[22] Morton salt

ZINC [7440-66-6]

The SDS (Sigma Aldrich) for zinc powder lists multiple potential GHS classified physical hazards: pyrophoric, evolves hydrogen when wet, explosible if dispersed in air. The DOT classifications are flammable solid (4.2) and emits flammable gases (hydrogen) when wet (4.3). Zinc dust explosions have been reported where there was attrition, such as grinding, and dispersion, such as sieving (Brethericks). Hydrogen is evolved when zinc is wetted with water 'especially under acid or alkaline conditions' (Brethericks). The CSB's Combustible Dust Hazard Study spreadsheet has two entries for 'zinc': one involved a small fire when dislodged dust, thought to contain zinc oxide, calcium carbonate or stearic acid, ignited. The second incident involved 'a mixer'; additional detailed information was 'not cleared'. Zinc (200 mesh or <74 micron) has ignition properties (e.g., ignition temperature of layers and dust clouds, MIE).

Four (4) zinc-based materials were subjected to evaluation: zinc powder, two (2) zinc-rich process dusts, and the finest fraction of dross after sieving. From Wikipedia, dross is "a mass of solid impurities floating on a molten metal or dispersed in the metal, such as in wrought iron". All samples were zinc-rich (at least greater than 50wt% Zn); particle morphology however ranged from the high surface area 'dusts' to particulate sieved from a dross sample. SEM images of commercially available zinc metal powder (99%, -325 mesh)[23] at 1,000 and 2,500 times magnification are shown in Figure A2-22. The powder consists of spherical particles with some agglomeration. The moisture content was low. Zinc powder did not ignite when exposed to a butane torch flame for 180 s or a propane-oxygen torch flame for 60 s (Fig. A2-23).

Figure A2-22 Zinc metal powder (American Elements, Lot No. 1871396147-413)



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[23] American Elements Lot No. 187396147-413

Figure A2-23 Zinc metal powder did not ignite
when exposed to butane or propane-oxygen torch flames

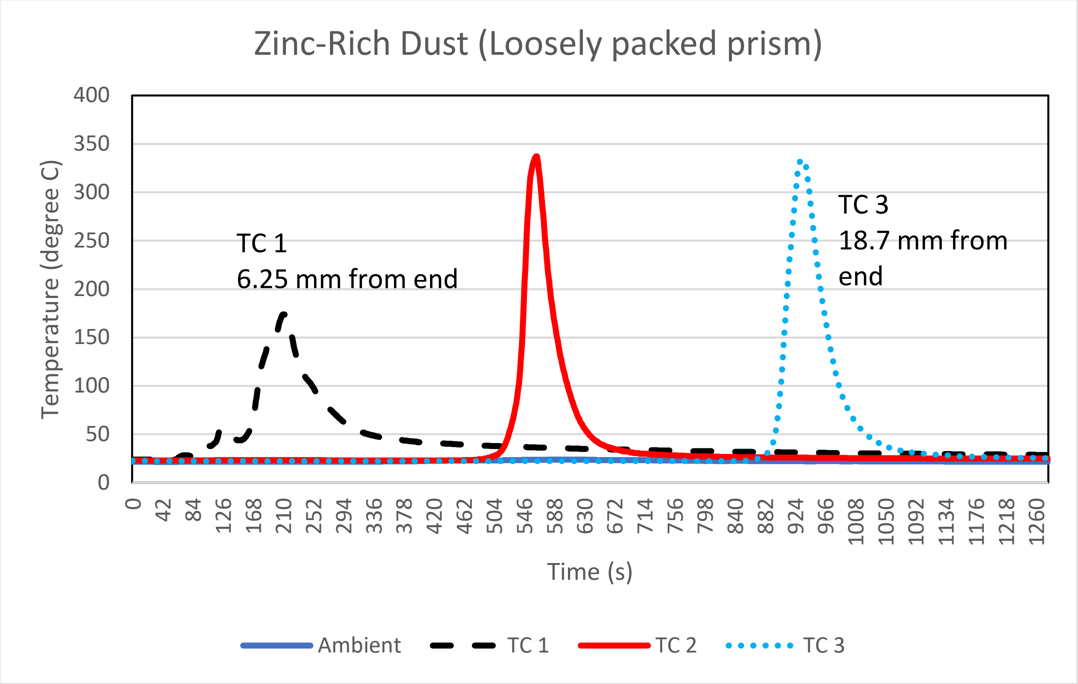
ZINC-RICH BAGHOUSE DUST

A zinc-rich baghouse dust was received, characterized, and subjected to testing. A supersack of the same dust was possibly involved in a warehouse fire storing other supersacks of process dust. The dust was uniform, matte gray in appearance, had a low moisture content (<1wt%), and a characteristically very high surface area. The average composition of the baghouse dust by EDS was 57 wt% zinc, 20 wt% carbon, 13 wt% oxygen, 8 wt% sodium, 1% chlorine, and trace aluminum. The dust was further characterized using thermal gravimetric analysis (TGA) with controlled heating (10C/min) in oxygen. The material started to decompose (lose mass) upon heating and continued until 20 wt% was lost by 755°C. The mass loss is most likely due to the volatilization of the carbon constituent in the dust.

When formed into a prismatic train on a cool, ceramic plate and one end exposed to a butane torch flame for 3 minutes, a smoldering front was established which propagated the entire length of the train (Fig. A2-24). The smoldering front had a trail of smoke; there was no visible flame. Beneath the surface was glowing orange. The burning rate ranged from **0.010 mm/s to 0.016 mm/s** with faster rates occurring for looser packed prismatic train. Smoldering combustion was confined to near the surface of the dust pile; therefore, thermocouples taped in place at/near the plate surface did not record actual burning temperatures (Fig. A2-25).

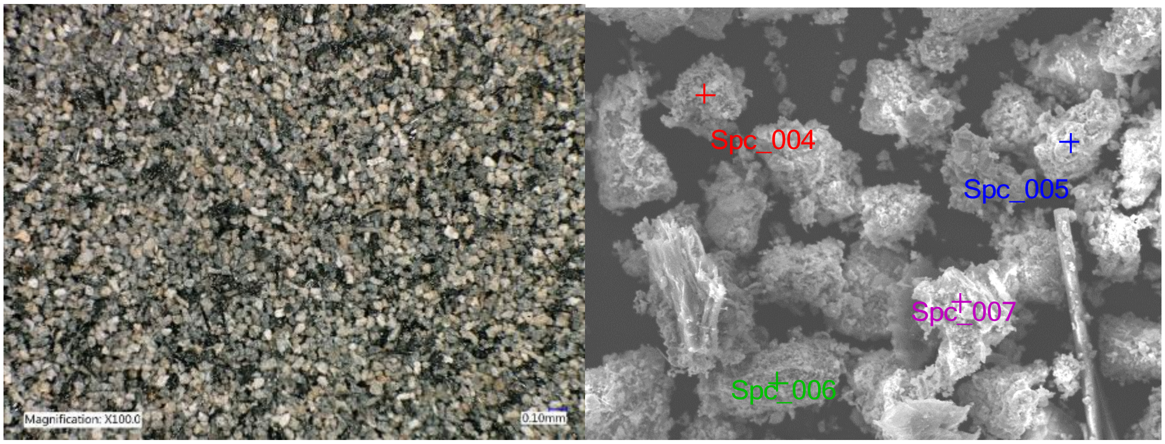
Figure A2-24 Smoldering combustion along prismatic train of zinc-rich baghouse dust

Figure A2-25 Temperature profile from baghouse dust



The dross sample was collected from a dross reclamation business. A typical dross sample was sieved, and the finest fraction had a -230+325 mesh particle size and range. The sample was analyzed by SEM EDS and found to contain, on average, 73 wt% Zn, 11 wt% C, 11 wt% O, 2.8 wt% Al, and trace (<1%) silicon, chlorine, potassium, calcium, iron, and titanium. The particles had a highly textured, irregular shape (Fig. A2-26).

Figure A2-26 Microscopic images of dross



The fine particle size dross (-230+325 mesh) was formed into a prismatic train on a cool ceramic plate and exposed to a butane torch at one end for 5 minutes; neither ignition or smoldering occurred. The opposite end was exposed to a propane oxygen torch flame for 60 seconds. Ignition or smoldering did not occur.

Zinc and zinc-rich mixtures are likely to be found in commerce from various processing. From NFPA 484, mixtures with >50 wt% metal are included in the scope of the Code. From tests performed, zinc and zinc-rich mixtures are not flammable solids per the existing DOT criterion. The physical hazards of zinc-rich particulate include combustible by smoldering if it contains elevated carbon content. Zinc's principal physical hazards, which may result in a fire or explosion, are conditional: exposed to air; exposed to water; exposed to other known reactants; dispersed in air.

Three forms of particulate zirconium[24] were subjected to characterization and testing: powder, milled fines, and rock. The influence of moisture content on the burning rate of zirconium powder was evaluated. Table A2-6 is a summary of the particulate zirconium burning rates.

Table A2-6 Summary of zirconium tests

Form	Size (mesh)	Moisture Content (%)	Ignition source	Burning Rate (mm/s)	No Trials
Powder (dry)	-50	0.2	Spark	5.3	3
Powder	-50	6.0	Spark	33.3	1
Milled fines 1	-	0.2	Butane torch	2.6	4
Milled fines 2	-	0.2	Butane torch	4.8	3
Rock (small)	-	2.0	Butane torch	1.2	3
Rock (large)	6	2.5	P/O	NI	1

Milled zirconium (dry) in a trough had a burning rate within the range of burning rate of zirconium in a prismatic train. A second form of milled zirconium (dry) had a consistently faster burning rate than the first form. The two sources of milled zirconium chemistry and particle size are compared in Table A2-7. The peak temperature recorded by K-type TC for all milled zirconium trials was 1,709°C.

Table A2-7 Chemistry and particle size distribution of two milled zirconium samples

Particle size	Sieve No.	Milled Zr 1
>3.35mm	+6	0.0
≤3.35>2mm	-6+10	0.0
≤2mm>1mm	-10+18	0.0
≤1mm>500um	-18+35	13.3
≤500um>300um	-35+50	12.1
≤300um>150um	-50+100	**35.5**
≤150um>90um	-100+170	20.7
≤90um>63um	-170+230	8.4
≤63um>45um	-230+325	5.9
≤45um	-325	4.2

POWDER

The dry commercially available powder (99%, -50 mesh[25]) was received in a plastic bottle packed under water. The zirconium powder was dried in a warming oven at 100°C after which it was dark gray metallic, lustrous, fine particulate in appearance. Two SEM images are shown in Figure A2-27; the powder consists of discrete particles which are irregular.

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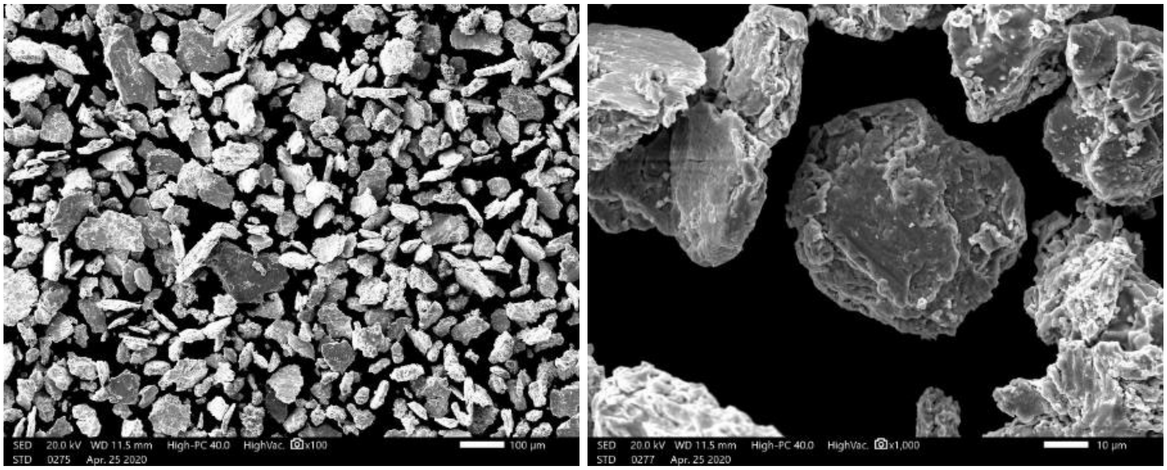
[24] The transportation assignment for zirconium powder is UN 1358 4.1 PG II.

[25] American Elements, COA, Zirconium Metal Powder, Lot No. 1901396147-325

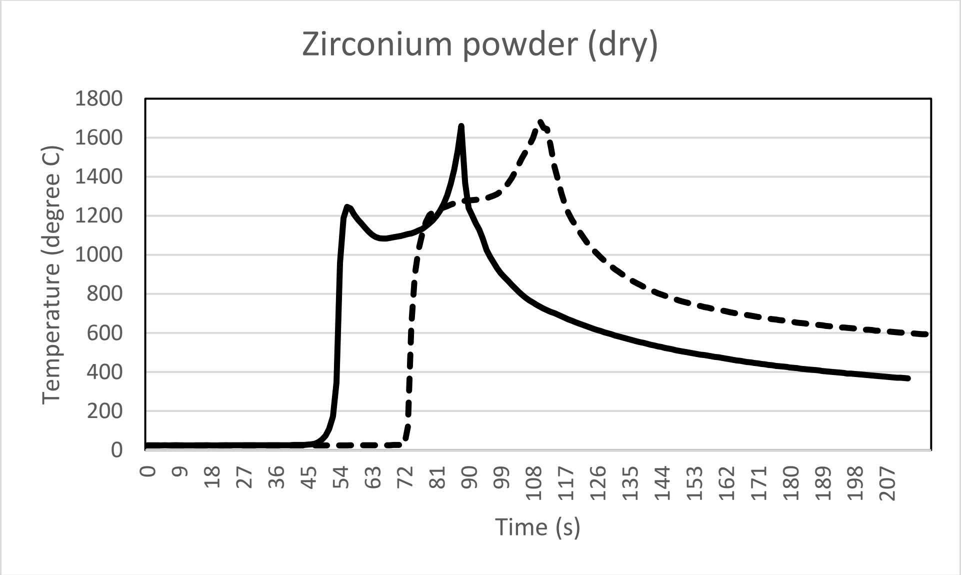
Figure A2-27 Zirconium powder after drying, at 100X (left) and 1000X (right)



When formed into a prismatic train, the powder ignited using a butane torch flame in two trials and with a spark in a third trial. The powder train ignited readily; burning propagated with a bright glow and orange flame. The flame continued to burn and the powder glow as combustion traveled from end to end as shown in Figure A2-28. After burning the full length of the prismatic train, the base of the prism would ignite and burn, suggesting the surface was burning first followed by the core of the material. The temperature profile of burning zirconium is bimodal reflecting this behavior. Peak temperatures recorded during burning ranged from 1,660°C to 1,741°C (Fig. 29). After combustion, the powder train retained elevated temperatures (~600°C). Upon cooling, it was a pale yellow dust.

Figure A2-28 Bright burning zirconium powder (dry) with persistent orange flame

Figure A2-29 Temperature profile of burning zirconium powder (dry)



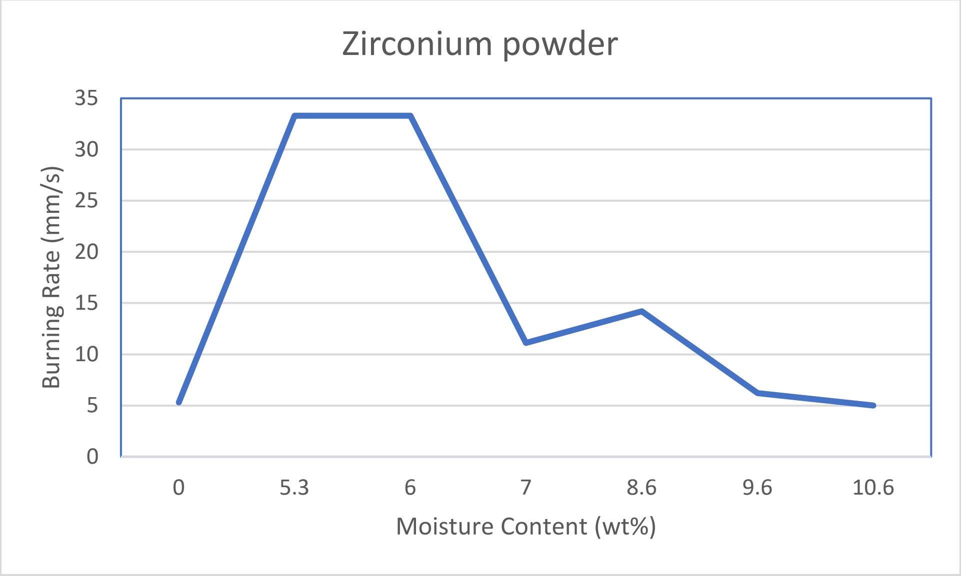
Burn rate testing was performed with dry powder as a prismatic train (three trials) and in a trough (1 trial). The burning rate of Zr in a prism was faster at 5.3 mm/s compared to 4mm/s in a trough. The temperature profile of the zirconium metal in a trough was also bimodal but less pronounced. The highest recorded temperature in the trough was 1,470°C.

Wet zirconium powder does not ignite and burn; this was confirmed by transferring wet powder from the shipping container to a trough. A butane torch was applied at one end for 180 seconds and a propane oxygen torch to the other end; ignition did not occur. It is known that moisture influences the ignition propensity and burning rate of zirconium. Zirconium powder was evaluated dry (0.2 wt%) and with between 5 and 11 weight percent moisture. Distilled water was spray applied to dry powder and thoroughly mixed. The resulting moisture content was measured using the moisture analyzer, and the damp zirconium powder was tested within minutes. Spray applying water, mixing, moisture content determination, and burn rate testing were repeated, resulting in increasing moisture content. The results are summarized in Table A2-8 and graphically in Figure A2-30. All of the moist zirconium burned with visibly larger flames and ejected burning particles. Zirconium powder with 5 to 6 wt% moisture was the most hazardous, resulting in a six-fold increase in burning rate.

Table A2-8 Zirconium powder dry and with increasing levels of water or moisture

Form	Moisture content (wt%)	Burn rate (mm/s)
Zr powder (wet)	100	NI
Zr powder (dry, trough)	0.2	4.0
Powder (prismatic train)	0.2	5.3
	5.3	33.3
	6	33.3
	7	11.1
	8.6	14.2
	9.6	6.2
	10.6	5.0

Figure A2-30 Burning rate of zirconium powder as a function of moisture content



MISCELLANEOUS METAL CONTAINING MIXTURES

Process dust with particulate metal can range in composition. Examples include particulate from dust collectors associated with various processing including shot blasting the surface of metal parts. Dust from one dust collector was characterized. The dust was dark gray, uniform, and had a fine particle size (mean diameter 97.6 microns). The average composition, determined by EDS, was 39% copper, 26% zinc, 14% phosphorous, 12% sulfur and 8% potassium. By definition, the dust is a metal-containing mixture with >65% metal. The dust had 0.5 weight percent moisture yet lost 10 weight percent when heated to 1,000°C in a muffle furnace.[26] When tested per the ASTM E1226 explosibility screening test in a 20-liter sphere and 5kJ igniter, the dust did not ignite and therefore was not in an explosible form.

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[26] Loss on ignition testing drives off organic and inorganic volatiles such as carbonates, etc.

APPENDIX 3. DETAILED DESCRIPTION OF INTERMEDIATE-SCALE TESTS

Representative microscope and SEM images of the four particulate titanium materials are shown in Figure A3-1. The floor sweep, or dust, was 98% Ti with 2% combined aluminum, silicon, chlorine, and iron. The sponge was 98.5% Ti and 1.5% carbon. The fines were titanium alloy (Ti 6V 4Al) contaminated with a ferrous material (0.4% Fe 1.8% Cr 4.2% Mo 2.6%C). The saw fines (after washing) were a Ti-Al alloy, iron, and oxide (85% Ti, 1.5% Al, 12% O, and 1% Fe). Overview photographs of the intermediate scale test set up with a prismatic train and a shallow drum are shown in Figure A3-2. A summary of the tests performed are included in Table A3-1.

Figure A3-1 Four particulate titanium used in intermediate-scale tests (from left: top and bottom): dust, -40 mesh sponge, fines and saw swarf.

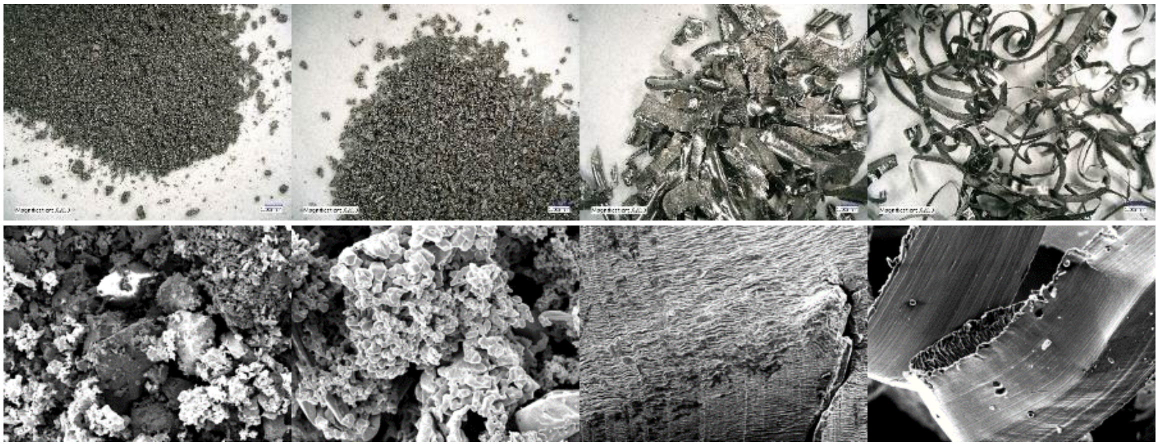

Figure A3-2 Intermediate scale test with prismatic train (L) and shallow drum (R)

Table A3-1 Summary of intermediate-scale tests performed

Form of Titanium	Total Trials	Liquid suppression F-500	Liquid suppression Firebane	Class D
Dust	2	x	x	
-40 Mesh Sponge	3	x	x	x
Fines	1	x		
Saw fines (as received)	1		x	

-40 MESH (75 MICRON) TITANIUM SPONGE

Three trials were performed with burning prismatic trains of titanium sponge (-40 mesh, 75 micron): one was extinguished with a Class D fire extinguisher, and two trials were subjected to two liquid suppression agents. The particulate metal was dull gray, free-flowing, or dry and not dusty. The lab conditions during the tests were 19°C with a 32 % relative humidity. Once ignited, the -40 mesh titanium sponge burned bright with a low, orange flame at the leading edge of burning; then flow flames, and glowing metal oxide persisted after the burning front passed.

In the first trial, a 1.2 m (48 in) prismatic train with 1.7 kg (3.9 lb) metal was formed and then ignited at one end with a MAPP gas torch. Ignition occurred within 10 s, and the metal continued to burn. The burning rate was regular at 0.38 m/min over the first 0.5 m (20 in) (e.g, between TCs 1 and 3). The FLIR recorded an average peak surface temperature of 1,460°C at the leading edge of burning. The average peak temperature recorded by the embedded S-type thermocouples was higher (1,624°C)[27]. The delay in time between the burning front was registered by the TC, and the peak temperature was 91 seconds.

The Class D fire extinguishing agent, a dry light-yellow powder, was discharged onto the burning metal for approximately 4 seconds when the local temperature recorded by the thermocouple reached 1,104° C. The powder covered the particulate metal, extinguishing the flames and the bright surface burning. The FLIR showed low surface temperatures where the powder covered the burning metal. Temperatures inside the pile decreased when the agent was applied but then slowly increased over time. Two minutes after applying the extinguishing agent, burning metal broke through along an edge of the applied extinguishing agent. A representative photograph showing the burning behavior of the -40 mesh titanium sponge is shown in Figure A3-3. A photograph after the application of the Class D extinguishing agent is shown in Figure A3-4. A temperature profile during the test is shown in Figure A3-5.

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[27] The average peak temperature does not include the peak temperature 1569°C reached after the Class D extinguishing agent was applied.

Figure A3-3 Burning behavior of -40 mesh sponge

Figure A3-4 Response of -40 mesh titanium sponge to application of Class D agent

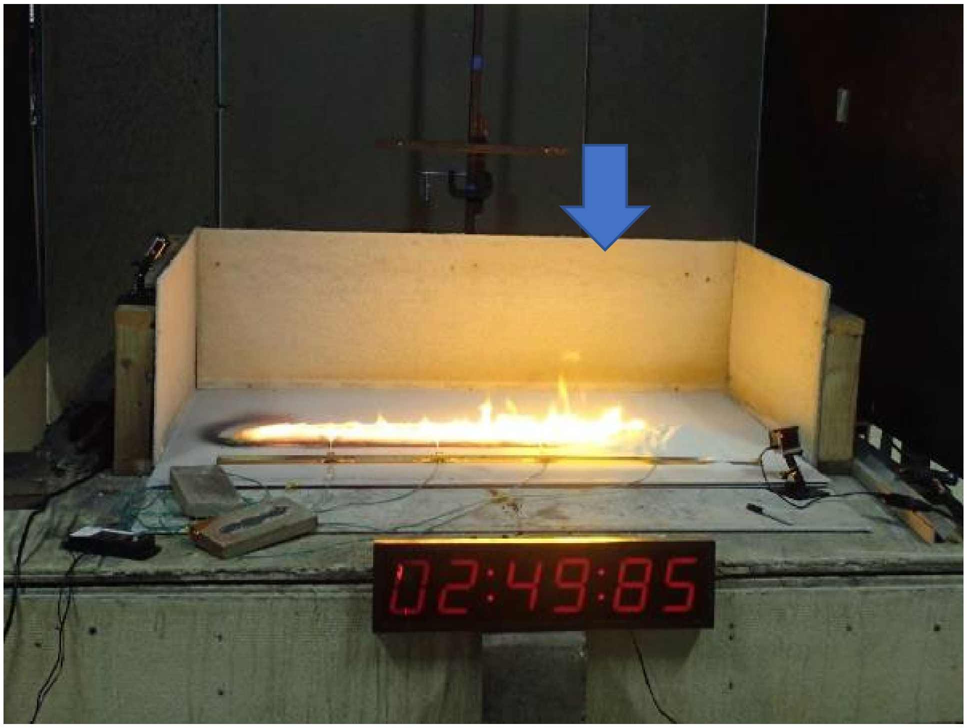
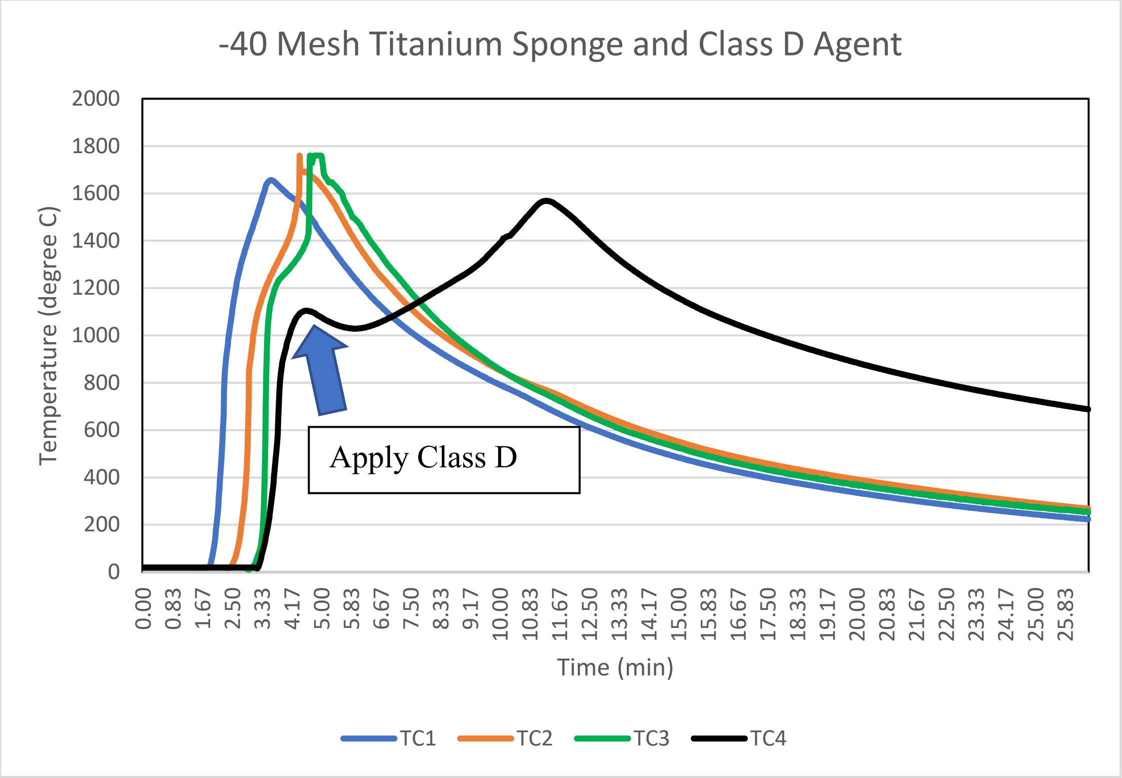


Figure A3-5 Temperature profile during test with titanium sponge and Class D agent



In a second trial, the sponge was arranged into a 1.2 m (48 in) train. The mass and depth of the particulate was 2.3 kg (4.6 lbs) and 3.5 cm (1.3 in), respectively. One of end of the particulate train ignited by a MAPP gas torch within 10 seconds. Once ignited, burning was sustained. Surface temperatures recorded by FLIR where highest at the leading edge of burning and averaged 1,475°C; the highest recorded was 1,543°C. From TC data, peak temperatures inside the burning mass ranged from 1,500°C to 1,712°C; the highest temperature occurring after the application of the liquid suppression agent. The burning rate from TC 2 to TC 4 was 0.6 m/min.

At 2 minutes 22 seconds, F-500 encapsulating agent (6%) was spray applied to the burning metal in the area of the fourth thermocouple. From the thermal imaging camera and temperature profile, the temperature decreased to approximately 1,050°C. When application ceased, temperatures slowly increased. A reaction between the burning metal and suppression agent occurred, resulting in burning metal, in the form of sparklers, to be jetted from or ejected by the wetted burning metal (Fig. A3-6). A second application of liquid suppression agent was applied near the end of the train. The total mass of liquid agent (F-500, 6%) applied was 1.7 kg (3.8 lbs). Where subject to F-500 (6%), the particulate metal train was black and crusted over. Figure A3-7 shows the temperature profile during the test.

Figure A3-6 Reaction between F-500 and burning titanium sponge

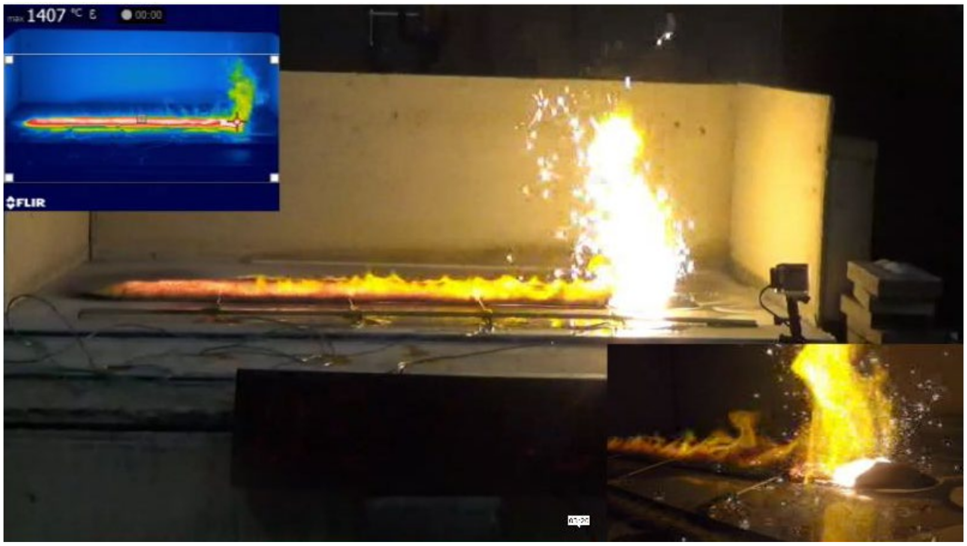
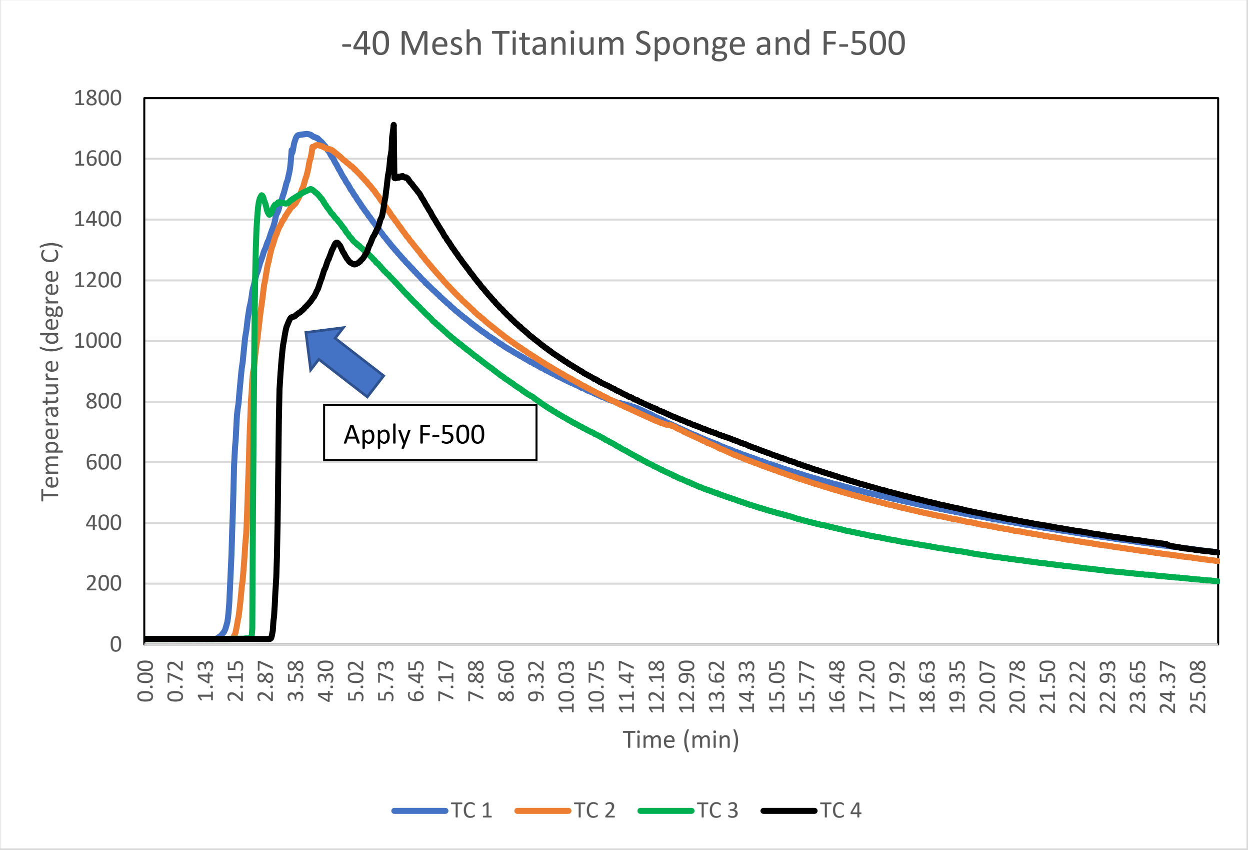


Figure A3-7 Temperature profile during testing with titanium sponge and F-500 agent



A third trial included a prismatic train with 2.1 kg (4.6 lbs) sponge that was 1.2 m (48 in) long, 10 cm (3.9 in) wide, and 3.5-4 cm (1.3in) in height. Ignition by the MAPP gas torch occurred within 6 seconds. In two instances, flaming brands ignited the sponge ahead of the burning front. The average surface and peak core temperatures while burning from both the FLIR and TCs was 1,475°C with peak inside temperatures ranging from 1,608 to 1,664°C. The burning rate was similar to previous trials.

Firebane was spray-applied when the burning metal front reached TC 4. The temperature of the burning metal locally decreased to 1,100°C and then slowly increased. A fireball or increased flames occurred upon application, adjacent to where the agent was applied on the powder train. More flaming combustion was observed where the burning metal was in contact with the liquid agent as compared to the far end of the train which was only glowing. The liquid agent appeared to boil where in contact with the burning metal. The unburned but wetted material ahead of the burning front had lower temperatures. When wetted, the leading edge of combustion burned with a white flame. While delayed, the metal continued to burn. A second application was applied at the end of the train. The total mass agent applied was 1.8 kg (4.1lbs).

Overview photographs during and after application of Firebane to the burning metal and a temperature profile are shown in Figures A3-8 and A3-9.

Figure A3-8 Reaction between burning titanium sponge upon (top) and after (bottom) Firebane application

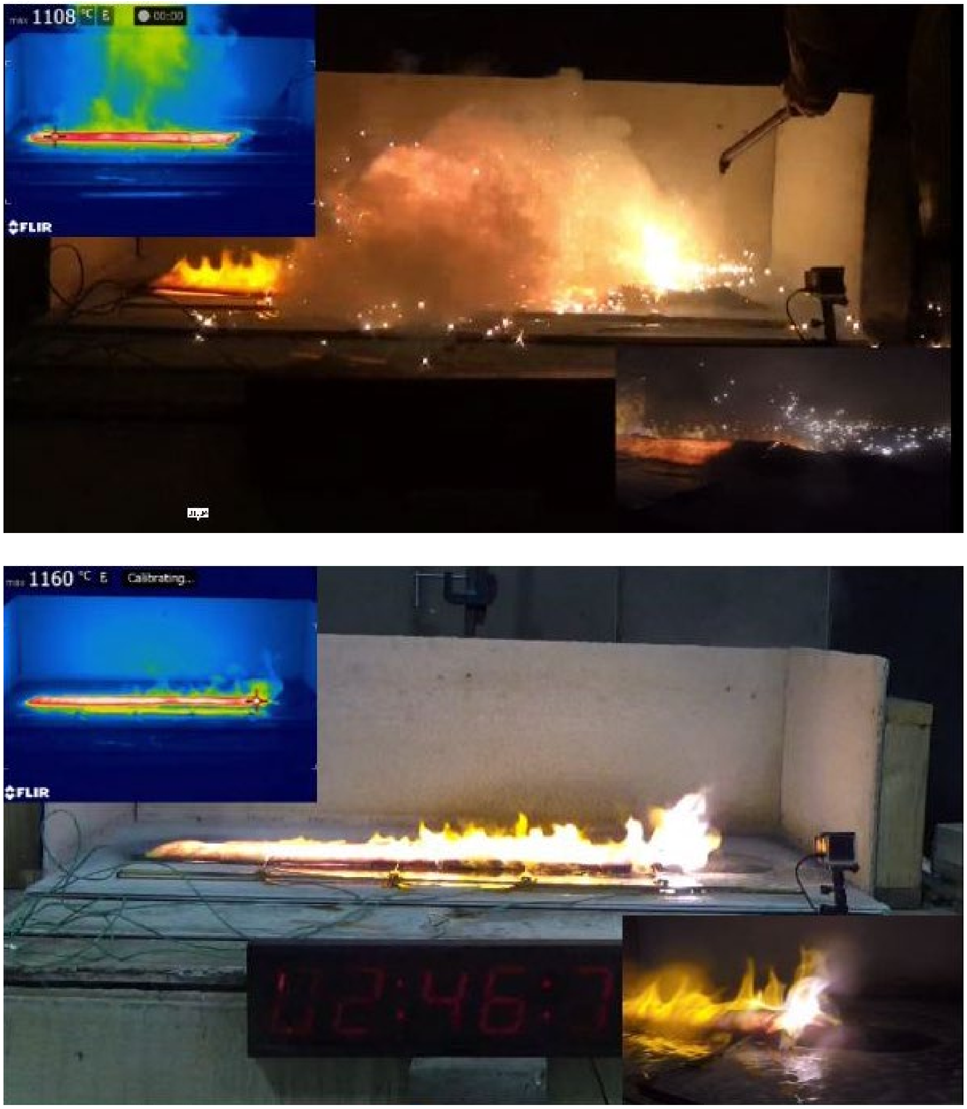
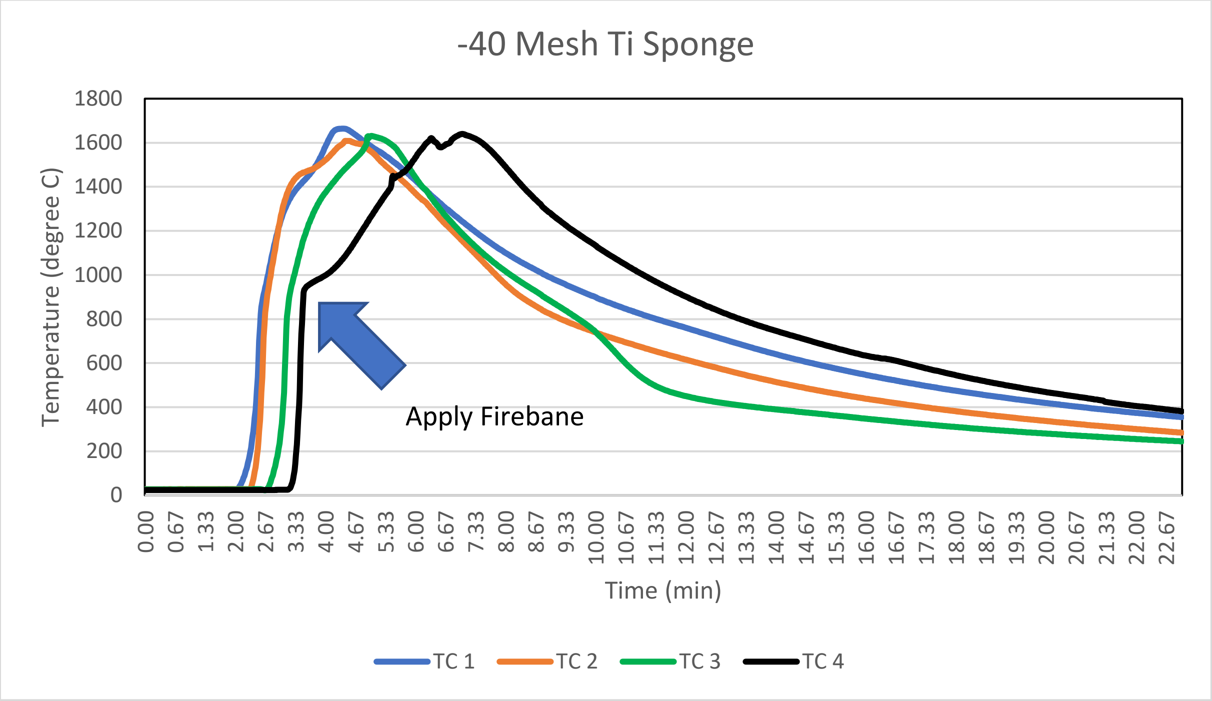
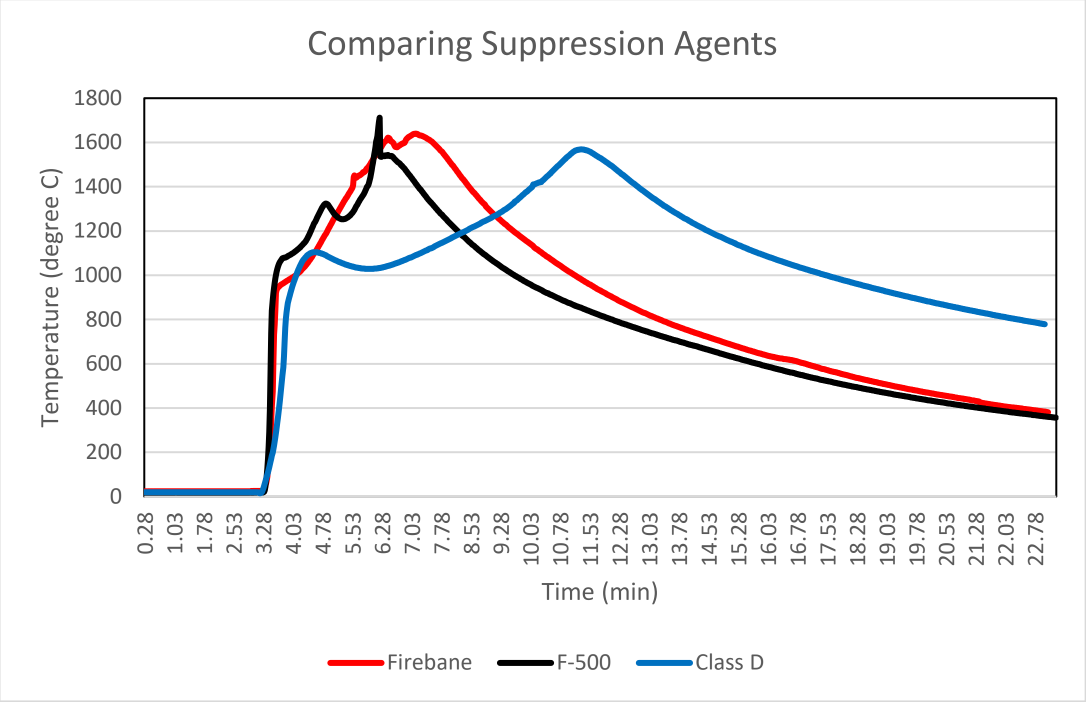


Figure A3-9 Temperature profile from titanium sponge trial with Firebane



The Class D and two liquid suppression agent temperature profiles when applied to titanium sponge are compared in Figure A3-10. The Class D extinguishing agent caused core burning metal temperatures to decrease and peak temperatures were delayed longer when compared to the liquid suppression agents.

Figure A3-10 Temperature profile of burning titanium sponge at TC 4 before, during, and after application of three extinguishing agents



TITANIUM DUST (FLOOR SWEEP)

Two intermediate scale tests were performed with a prismatic train and a drum of titanium dust. The particulate material was a fine powder, dull silver-gray in color, with a low moisture content, an irregular particle shape, and narrow particle size range.

The titanium dust material train was ignited using a MAPP gas torch applied to one end. The material ignited within 90 seconds and continued to burn the entire length. The thermal imaging video camera showed an average surface temperature of 1,300°C during burning with a peak surface temperature reaching 1,450°C. The S-type thermocouples embedded in the metal registered peak temperatures greater than 1,600°C as the burning front passed. The burning rate was slow, on the order of 0.03 meter per minute.

The F-500 suppression agent was applied for 5 seconds on two occasions. Application of the liquid suppression agent resulted in a temperature decrease from 1,300°C to 450°C. When the application ceased, the temperature of the metal started to increase, almost immediately, up to 1,140°C. A second application resulted in temperatures decreasing to 378°C and slowing of the propagation of burning but not extinguishment. An application of sodium chloride (salt) caused the burning to cease but temperatures remained around 930°C. A representative photograph is shown in Figure A3-11. The decrease in temperature upon application of the suppression agent observed in the thermal image was recorded by thermocouples embedded in the train (Fig. A3-12).

Figure A3-11 Burning behavior of titanium dust before (top) and after (bottom) F-500 application

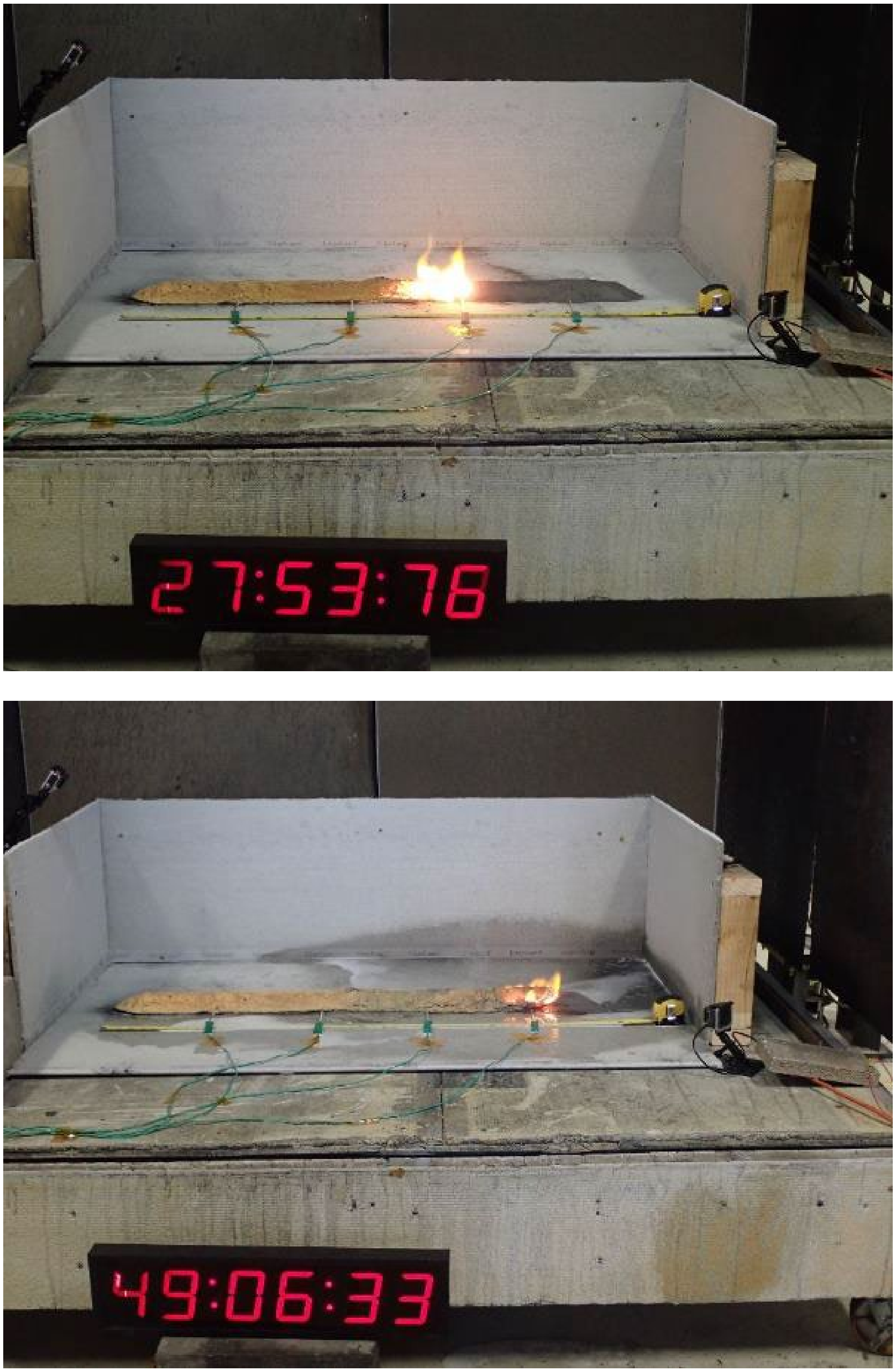
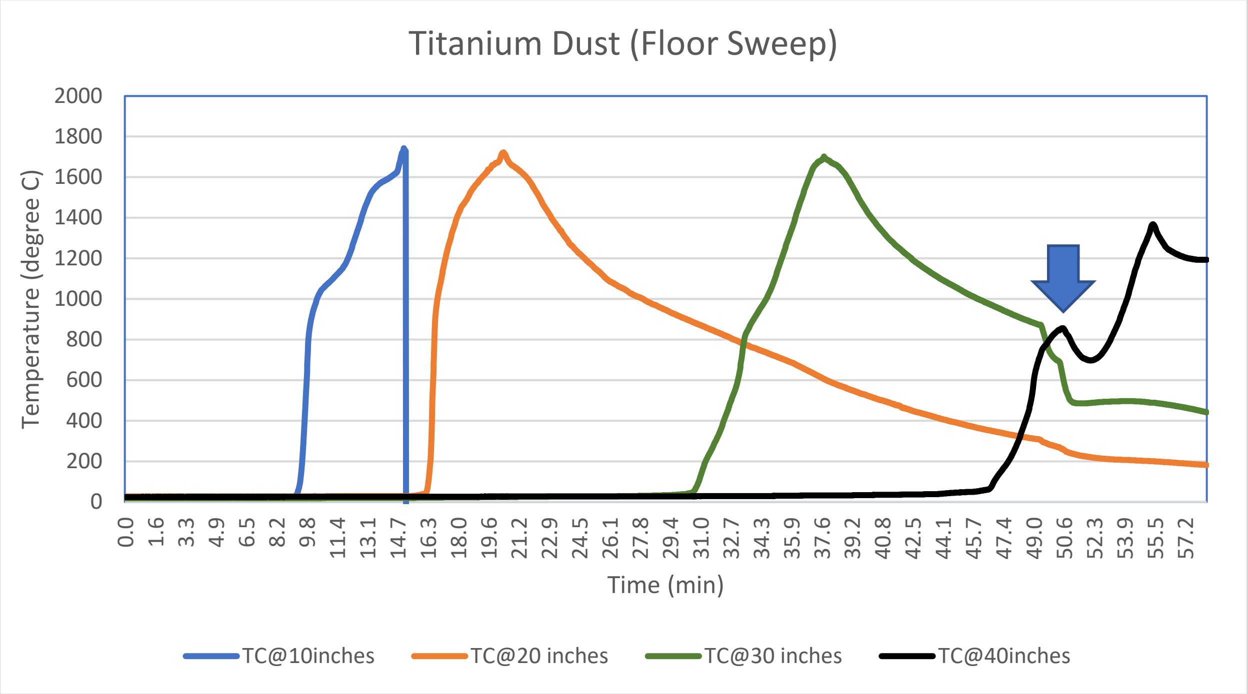


Figure A3-12 Temperature profile during test with titanium dust and F-500



The same material (5.2 kg, 11.9 lbs) was added to a shallow steel drum (9.2 cm (3.6in) deep; 27.9 cm (11 in) diameter) and ignited with a road flare. Approximately 60 percent of the shallow drum volume was dust. Thermocouples were embedded in the material from the top sides of the drum. The video and thermal imaging cameras showed elevated temperatures spread over and through the drum wall.

When a majority of the metal appeared to be burning, the F-500 suppression agent was added. Some of the suppression agent accumulated in the drum, which then appeared to boil and evolve a white gaseous cloud. The particulate metal appeared to have crusted over when breakthrough ignitions occurred, indicating the metal re-ignited and continued to burn. A second application of the suppression agent resulted in a similar behavior. The third application doused the burning metal. The total weight of F-500 suppression agent added to the shallow drum was 3 kg (6 lbs). Representative photographs during the test are shown in Figure A3-13.

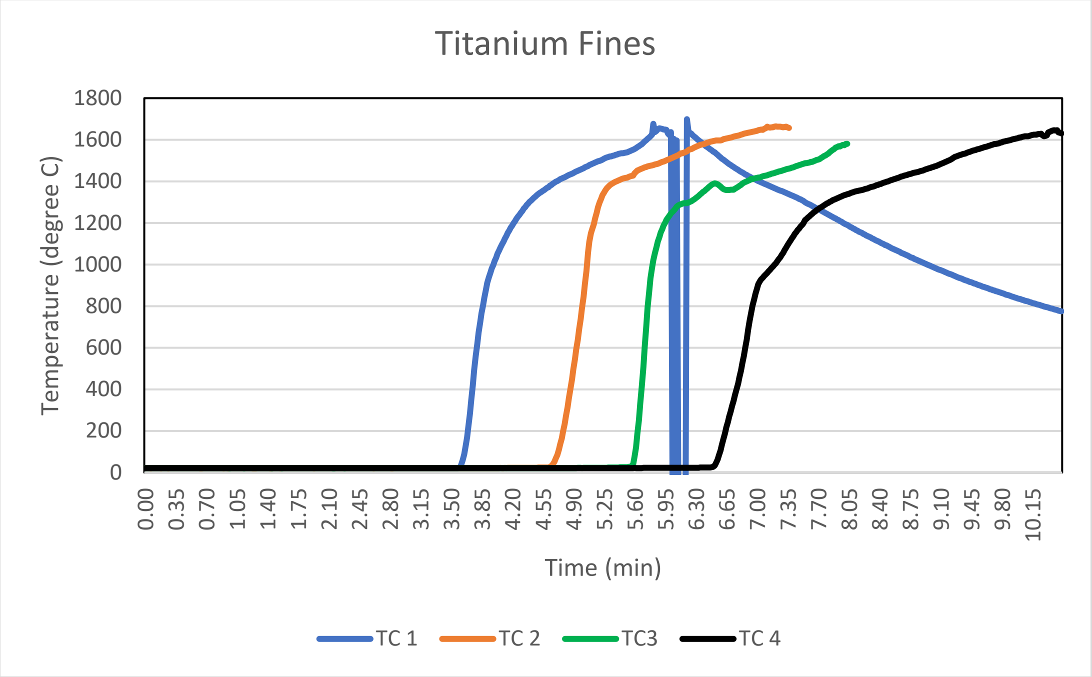
Figure A3-13 The response of titanium dust in a drum after application of F-500

TITANIUM FINES

Titanium fines consisted of discrete, metallic metal shavings. The particulate was arranged into a prismatic train. One end of the train was ignited using a MAPP gas torch. Once ignited, combustion continued. The average burning rate was 0.24 m/min. The temperatures inside the pile, which increased to peak temperatures at least 2 to 3 minutes after the burning front passed, caused the TCs to melt open. Representative photographs of the burning fines and the response when F-500 was applied are shown in Figure A3-14. A temperature profile is shown in Figure A3-15. The temperature inside the pile caused the thermocouples to open (e.g., T>1,750°C).

Figure A3-14 Titanium fines while burning (top) and after (bottom) F-500 was applied for 5 seconds

Figure A3-15 Temperature profile during test with titanium fines



SAW SWARF

Saw swarf were received damp with a cutting fluid. The saw swarf had a Brillo-pad type texture and was brittle or frangible. The saw swarf was tested as-received. Saw swarf (3.4 lbs, kg) were arranged into a continuous train that was approximately 6.5 cm in height and 6-inches wide. It required at least 30 seconds application of a MAPP gas torch to sustain burning without self-extinguishing; ignition was forced to occur at the right end of the train. Once ignited, burning was characterized as a ‘pre-heating’ of the saw swarf followed by an advancing bright burning with 0.4 m tall orange flames. After the burning front passed, the metal retained heat but did not exhibit flames or glowing.

Firebane was applied to the burning metal in the area of the fourth thermocouple for 5 seconds. After ceasing application, there was an increase in burning with tall flames (~0.8m) for 3 seconds. Burning continued at the pile, but the burning metal did not advance. The quantity of Firebane discharged was 0.8 kg (1.8 lbs). Representative photographs of the burning saw fines and the response when Firebane was applied are shown in Figure A3-16. A temperature profile is shown in Figure A3-17.

Figure A3-16 Behavior of burning saw fines (top) and response to Firebane (bottom)

Figure A3-17 Temperature profile of burning saw fines and application of Firebane